EXPERIMENTAL AND THEORETICAL INVESTIGATIONS ON OPTICAL ROTATORY POWER

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ABSTRACT

The optical rotatory power of a fluid system of molecules is calculated. The result is the same as obtained by previous investigators using similar but less satisfactory arguments. Various means of calculating the optical activity of a substance are discussed, one previously used by Kirkwood being employed to discuss theoretically the absolute configurations of trans-2,3-epoxybutane, 1,2-dichloropropane and 1,2-dibromopropane. An experimental investigation of the molecular structure of 1,2-dichloropropane by electron diffraction methods is described.

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SECTION I

INTRODUCTION

The rotation of the plane of polarization of a beam of linearly polarized light during its passage through a material medium was first observed by Arago[1] in 1811, in crystalline quartz. In 1815 Biot and Seebeck[2], during experiments designed to investigate the effect of surrounding media on the optical rotatory power of quartz, noted that several liquids as well as aqueous solutions of certain substances also exhibited the same ability to rotate the plane of polarization of the light beam. In 1817 Biot[3] observed optical activity in the vapor state of certain substances.

Pasteur[4] in 1848 made the very important and famous discovery of the existence of two isomers of sodium ammonium tartrate, differing in the signs of their optical rotations, and having crystal habits related to each other as mirror images. He produced these by crystallization from the racemic mixture at temperatures slightly below room temperature, this being the first resolution of a racemic mixture. From the experimental evidence, Pasteur[5] empirically deduced as the criterion for the possibility of existence of optical isomers the non-superposability of the molecule with its mirror image. He realized at the same time the necessity of using three-dimensional molecular models, but did not propose a specific geometrical structure. The latter was done nearly

simultaneously by van't Hoff[6] and LeBel[7], with their famous suggestion of the tetrahedral carbon atom, and their correlation of optical activity with the presence of an asymmetric carbon atom in the molecule. Both experiment and theory have since shown that the latter requirement for optical activity is too special, the correct one being the more general criterion of Pasteur.

Soon after the discovery of optical rotatory power, Fresnel[8] proposed a theoretical explanation for the phenomenon in crystals such as quartz, where the rotatory power disappears on fusion or solution in optically inactive solvents. He postulated a helicoidal arrangement of the atoms, there being two such arrangements identical except for one being right-handed, the other left-handed. Since then modern x-ray crystallography has indeed confirmed this postulate of Fresnel. With this hypothesis, he showed that the refractive indices of a given (right- or left-handed) helicoid would be different for right and left circularly polarized light, and that this would result in the rotation of the plane of polarization of a linearly polarized light beam.

Such an explanation is obviously not applicable to those substances exhibiting optical rotation in the liquid or vapor states, and indeed an adequate theory for these cases was much longer in forthcoming. Drude[9] developed a theory in which the electrons in the molecule were supposed constrained to vibrate in helicoidal paths.

Besides the artificiality of the model, it has since been shown by Kuhn[10] that Drude's calculations contained an error, and that the model correctly treated gives no optical activity. A satisfactory explanation was first found nearly simultaneously by Born[11], Oseen[12] and Gray[13]. These authors perceived that it was essential to consider the retardation of the light wave over the molecular dimensions; when this was taken into account optical rotatory power was found to be a natural consequence of the molecular theories then extant. Born and Oseen based their theories on the classical coupled-oscillator models of the dispersion theory, making no specific correlations with the molecular structure. Gray, on the other hand, considered a specific molecule, postulating harmonic oscillators located in particular groups or atoms in the molecule, and developed the theory in terms of the polarizability of these groups. The Born-Oseen and the Gray theories are similar in principle, differing only in the specific assumptions made about the model. Gans[14] has pointed out several errors in the original Born-Oseen theory. A specialization of this classical theory has been extensively applied by Kuhn. A brief discussion of his method will be given later. The polarizability theory has been improved by de Mallemann[15] and by Boys[16] but usually unwarranted assumptions of optically isotropic groups in the molecule have been made.

A general quantum mechanical formulation of the problem of optical activity was given by Rosenfeld[17] in 1929.

The quantum mechanical foundations of the Rosenfeld argument naturally are free from the defects of the classical oscillator theories, and the general formula obtained is the appropriate starting point for discussions of the optical rotatory power of specific quantum mechanical systems.

Here we shall devote ourselves first (Section II) to the derivation of the Rosenfeld formula, following the general lines of Rosenfeld's argument, but treating certain points in greater detail. In Section III the generalized polarizability theory of Kirkwood will be described, and application made to the determination of the absolute configurations of several optically active compounds. The one-electron theory of Eyring and his co-workers and Kuhn's application of the classical coupled-oscillator theory will be briefly discussed in Section IV. There we shall also give a brief summary of the problem of the absolute configuration as it stands at present. Section V will describe an electron diffraction investigation of the molecular structure of 1,2-dichloropropane, one of the substances considered in Section III.

SECTION II

QUANTUM MECHANICAL AND STATISTICAL MECHANICAL THEORY OF THE OPTICAL ACTIVITY OF FLUID SYSTEMS

Introduction

The published derivations[17,18,19] of the Rosenfeld formula proceed in the following scheme. The effective external electromagnetic field on the molecule is taken to be that of a simply periodic plane light wave; the induced electric and magnetic moments are then calculated, an average being taken over the angular orientations of the molecule with respect to the light wave, treating all orientations as equally probable. This last step is introduced since we desire to calculate the induced moments for the gaseous or liquid states in the absence of other orienting electric or magnetic fields, rather than in the presence of such fields or for the crystalline state. The Lorenz-Lorentz relation for the effective field in terms of the macroscopic electric intensity and polarization is then introduced in a not wholly consistent way to obtain the polarization and magnetization in terms of the macroscopic field vectors. Using these equations as material equations and Maxwell's equations for a dielectric medium, it may be shown that the medium exhibits circular double refraction and therefore optical activity.

It is to be noted first of all that in a fluid system of polarizable particles through which a plane light wave is propagating, the electric (and magnetic) field acting on a given molecule at a given instant does not correspond

to a simply periodic plane wave, in spite of the fact that this may be the character of the incident wave. This is due to the radiation fields of the induced moments in the other molecules. If the other molecules were stationary the effective field would be simply periodic with the frequency of the incident wave, though not in general plane wave in form, depending on the configuration of the molecules. The actual motions of the molecules in a fluid system result in an extremely complicated time dependence of the effective field at a given molecule. However, for frequencies in the range of visible light, the electromagnetic field due to the incident light will have completed many cycles over a period of time required for appreciable variation in the field due to the molecular motions. Consequently we may to a good approximation treat the induced moments as simply periodic with the frequency of the incident light wave.

The average electromagnetic field at a given molecule is a plane wave, as indicated by experiment and demonstrated theoretically by Lundblad[20] for the case of an infinite medium in which the molecules composing the system are optically isotropic. However, such a quantity as the average of the curl of the electric field at a given molecule will not in general be identical with the curl of the average electric field at the molecule, since the statistical weighting function will in general depend on the coordinates of the given molecule, as well as those of the

other molecules. As will be seen later, such quantities as those of the former type enter into the theory, so that it is essential to avoid the assumption of plane wave dependence of the instantaneous effective electric field. The distinction between the two types of quantities may also be drawn from arguments based on the Lorentz cavity, as was pointed out by Gans[14]; however, because of the added clarity of arguments based on statistical mechanics it seems preferable to follow the latter reasoning, especially since the exact nature of the assumptions involved may be more clearly seen.

Accordingly, we will first (Part I) develop the quantum mechanical formulas for the electric and magnetic moments induced in a molecule initially (before the application of the electromagnetic field) in a given quantum state. The electromagnetic field will be assumed to be simply periodic, but otherwise arbitrary, except that it must satisfy Maxwell's equations for a vacuum. Having done this, the remaining problem will be the statistical mechanical one of averaging the resulting formulas over the various quantum states of the system.

Part I: Quantum mechanical theory

We formally suppose the Schrödinger equation to have been solved for the molecule in the field-free condition; the time-dependent Schrödinger equation is then set up and solved by the method of variation of constants, the

expansion being in the eigenfunctions of the Hamiltonian in the absence of the field, treating the part of the Hamiltonian arising from the presence of the field as a perturbation. If we denote the complete Hamiltonian (including the field terms) by H, the time-dependent Schrödinger equation is

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad . \tag{1}$$

In accordance with the above, we write

$$H = \mathring{H} + H'(t), \tag{2}$$

where $\mathring{H}$ is independent of time, and is the Hamiltonian for the system in the absence of the electromagnetic field; H' (t) is the time-dependent term arising from the presence of the light field. To obtain a solution of equation (1) we write

$$\Psi = \sum_K c_K(t)\, \mathring{\psi}_K e^{\frac{-i\mathring{E}_K t}{\hbar}} \quad , \tag{3}$$

where the $\mathring{\psi}_K$ are independent of time, and satisfy the equation

$$\mathring{H}\mathring{\psi}_K = \mathring{E}_K \mathring{\psi}_K \quad . \tag{4}$$

Substitution of equation (3) into (1) with use of (4) then gives, after the familiar multiplication by any arbitrary $\mathring{\psi}_j$ and integration over configuration space, the well-known

system of equations

$$\frac{dc_j}{dt} = \frac{1}{i\hbar} \sum_K c_K(t) H'_{jK} e^{2\pi i \mathring{\nu}_{jK} t}, \quad j = 1, \cdots \tag{5}$$

where H'_{jK} is the usual matrix element of $H'(t)$ in the representation of the eigenfunctions of $\overset{o}{H}$ and $\mathring{\nu}_{jK} = \frac{1}{h}(\mathring{E}_j - \mathring{E}_K)$.

We suppose $H'(t)$ to be small, as can evidently be done by making the light intensity sufficiently weak. The system of equations (5) is then solved approximately by replacing the coefficients $c_K(t)$ on the right-hand side by their values $c_K(t_o)$ at some initial time t_o, the latter values being supposed known from the statement of the problem. If we also specialize to the case of present interest, that is, periodic $H'(t)$, we may write

$$H'(t) = Ae^{2\pi i \nu t} + A^+ e^{-2\pi i \nu t}, \tag{6}$$

where A is independent of the time. It is necessary, however, to consider the initial condition. In order to avoid the appearance of incoherent terms depending on the manner of turning on the perturbation at time t_o, we will use a device due to Born[21] and write, in place of equation (6),

$$H'(t) = \left(Ae^{2\pi i \nu t} + A^+ e^{-2\pi i \nu t}\right) e^{\sigma t}, \quad t \geq t_o$$

$$= 0, \quad t \leq t_o \tag{7}$$

where σ is real and positive. This represents an approximately periodic perturbation of slowly increasing amplitude; by suitable choice of σ we will obtain the purely periodic case of equation (6) in the limit as σ approaches zero and t_o approaches minus infinity. We further suppose that at t_o the system is known to have been in quantum state i, with eigenfunction $\mathring{\psi}_i$. Thus

$$c_K(t_o) = \delta_{iK} \quad . \tag{8}$$

Using equations (7) and (8) in (5), we obtain

$$\frac{dc_j}{dt} = \frac{1}{i\hbar}\left(\mathring{A}_{ji}e^{2\pi i\nu t} + \mathring{A}^{\dagger}_{ji}e^{-2\pi i\nu t}\right)e^{\sigma t + 2\pi i\mathring{\nu}_{ji}t} \quad , \tag{9}$$

an approximation valid for t not too far removed from t_o. Integrating equation (9) between t_o and t, one finds

$$i\hbar\left(c_j(t) - \delta_{ij}\right) =$$

$$\left(\frac{\mathring{A}_{ji}e^{2\pi i(\mathring{\nu}_{ji}+\nu)t}}{2\pi i(\mathring{\nu}_{ji}+\nu)+\sigma} + \frac{\mathring{A}^{\dagger}_{ji}e^{2\pi i(\mathring{\nu}_{ji}-\nu)t}}{2\pi i(\mathring{\nu}_{ji}-\nu)+\sigma}\right)e^{\sigma t}$$

$$- \left(\frac{\mathring{A}_{ji}e^{2\pi i(\mathring{\nu}_{ji}+\nu)t_o}}{2\pi i(\mathring{\nu}_{ji}+\nu)+\sigma} + \frac{\mathring{A}^{\dagger}_{ji}e^{2\pi i(\mathring{\nu}_{ji}-\nu)t_o}}{2\pi i(\mathring{\nu}_{ji}-\nu)+\sigma}\right)e^{\sigma t_o} \quad . \tag{10}$$

Now σ and t_0 are at our disposal, and the Born device is to allow σ to approach zero and t_0 to approach minus infinity in such a way that σt_0 approaches minus infinity, for instance by setting $\sigma = \varepsilon$, $t_0 = -\frac{1}{\varepsilon^2}$, where $\varepsilon > 0$, and allowing ε to approach zero. Then σt approaches zero, σt_0 approaches minus infinity, and in the limit we have

$$c_j(t) - \delta_{ij} = -\frac{1}{h}\left(\frac{\mathring{A}_{ji} e^{2\pi i(\mathring{\nu}_{ji}+\nu)t}}{\mathring{\nu}_{ji}+\nu} + \frac{\mathring{A}^{\dagger}_{ji} e^{2\pi i(\mathring{\nu}_{ji}-\nu)t}}{\mathring{\nu}_{ji}-\nu}\right). \tag{11}$$

Substituting in equation (3) we obtain as the first order equation for the wave function under the influence of the perturbation

$$\Psi_i = \mathring{\psi}_i e^{-2\pi i \mathring{\nu}_i t} - \frac{1}{h}\sum_{\kappa}\left(\frac{\mathring{A}_{\kappa i} e^{-2\pi i(\mathring{\nu}_i-\nu)t}}{\mathring{\nu}_{\kappa i}+\nu} + \frac{\mathring{A}^{\dagger}_{\kappa i} e^{-2\pi i(\mathring{\nu}_i+\nu)t}}{\mathring{\nu}_{\kappa i}-\nu}\right)\mathring{\psi}_{\kappa}, \tag{12}$$

where the subscript i has been added to Ψ to indicate that it corresponds to that state of the perturbed system

which is derived from the ith state of the unperturbed system.

The diagonal matrix elements of an observable f in the perturbed system are then given by

$$f_{ii} = \mathring{f}_{ii} + \sum_{K} \left(\frac{\mathring{A}_{iK}\mathring{f}_{Ki}}{h(\mathring{\nu}_{iK}+\nu)} - \frac{\mathring{f}_{iK}\mathring{A}_{Ki}}{h(\mathring{\nu}_{Ki}+\nu)} \right) e^{2\pi i\nu t} +$$

$$\sum_{K} \left(\frac{\mathring{A}^{\dagger}_{iK}\mathring{f}_{Ki}}{h(\mathring{\nu}_{iK}-\nu)} - \frac{\mathring{f}_{iK}\mathring{A}^{\dagger}_{Ki}}{h(\mathring{\nu}_{Ki}-\nu)} \right) e^{-2\pi i\nu t} , \tag{13}$$

where the zero over a matrix element of f indicates that the matrix element is in the representation in which $\mathring{H}$ is diagonal.

The Hamiltonian for a system of particles in an electromagnetic field is

$$H = \mathring{H} + \sum_{T} \left\{ \frac{-e_T}{2m_T c} \left(\vec{p}_T \cdot \vec{A}_T + \vec{A}_T \cdot \vec{p}_T \right) + \frac{e_T^2}{2m_T c^2} \vec{A}_T^2 + e_T \phi_T \right\} \tag{14}$$

where $\mathring{H}$ is the Hamiltonian in absence of the field; $\vec{A}_T$ and ϕ_T are respectively the vector and scalar potentials

at the position of particle τ, e_τ and m_τ are respectively the charge and mass of particle τ; and $\vec{p}_\tau$ is its momentum operator. The sum goes over all particles of the system. Condon, Altar, and Eyring[22] have shown that the neglect of contributions of the particle spins of the form $\vec{S}_\tau \cdot (\nabla \times \vec{A})_\tau$ in the above expression is justified in discussing the phenomenon of optical rotatory power.

Since we are interested in forming a linear theory and since the perturbing field is supposed to be small, we neglect the term in $\vec{A}_\tau^2$. We then have

$$H'(t) = \sum \left\{ \frac{-e_\tau}{2m_\tau c} \left(\vec{p}_\tau \cdot \vec{A}_\tau + \vec{A}_\tau \cdot p_\tau \right) + e_\tau \phi_\tau \right\}. \tag{15}$$

In accordance with our supposition of a simply periodic field we write

$$\vec{A} = \frac{1}{2}\left(\mathring{\vec{A}} e^{2\pi i \nu t} + \mathring{\vec{A}}^* e^{-2\pi i \nu t} \right),$$

$$\phi = \frac{1}{2}\left(\mathring{\phi} e^{2\pi i \nu t} + \mathring{\phi}^* e^{-2\pi i \nu t} \right), \tag{16}$$

where $\mathring{A}$ and $\mathring{\phi}$ are functions of the coordinates but not of the time. Substituting equation (16) into (15), and comparing with (6) we find

$$A = \sum \left\{ \frac{-e_\tau}{2m_\tau c} \frac{1}{2} \left(\vec{p}_\tau \cdot \mathring{\vec{A}}(\vec{r}_\tau) + \mathring{\vec{A}}(\vec{r}_\tau) \cdot \vec{p}_\tau \right) + \frac{1}{2} e_\tau \mathring{\phi}(\vec{r}_\tau) \right\},$$

$$A^+ = \sum \left\{ \frac{-e_\tau}{2m_\tau c} \frac{1}{2} \left(\vec{p}_\tau \cdot \mathring{\vec{A}}^*(\vec{r}_\tau) + \mathring{\vec{A}}^*(\vec{r}_\tau) \cdot \vec{p}_\tau \right) + \frac{1}{2} e_\tau \mathring{\phi}^*(\vec{r}_\tau) \right\}. \tag{17}$$

The next step is that of introducing the Taylor expansions

$$\mathring{\vec{A}}(\vec{r}_\tau) = \mathring{\vec{A}}(\vec{R}) + \vec{r}_\tau \cdot \nabla_{\vec{R}} \mathring{\vec{A}}(\vec{R}) + \cdots\cdots ,$$

$$\mathring{\phi}(\vec{r}_\tau) = \mathring{\phi}(\vec{R}) + \vec{r}_\tau \cdot \nabla_{\vec{R}} \mathring{\phi}(\vec{R}) + \frac{1}{2} \vec{r}_\tau \vec{r}_\tau : \nabla_{\vec{R}} \nabla_{\vec{R}} \mathring{\phi}(\vec{R}) + \cdots , \tag{18}$$

where we will neglect the higher terms of the series. $\vec{R}$ is the vector position of the center of mass of the molecule with respect to a convenient fixed external origin; $\vec{r}_\tau$ is the vector position of the particle τ of the molecule with respect to the molecular center of mass. The double dot multiplication of two dyadics is defined by the equation

$$\underline{\underline{A}} : \underline{\underline{B}} = \sum_{i,j=1}^{3} A_{ij} B_{ji} \tag{19}$$

With respect to the field vectors $\vec{E}$ and $\vec{B}$, inspection of equation (18) shows that we are retaining the first two

terms in the expansion of $\vec{E}$, but only the first term of $\vec{B}$. This means that we are considering the retardation of the electric intensity, but neglecting the retardation of the magnetic induction.

Introduction of equation (18) into (17) leads to

$$A = \sum_\tau \left\{ \frac{-e_\tau}{2m_\tau c} \mathring{\vec{A}}(\vec{R}) \cdot \vec{p}_\tau - \frac{e_\tau}{2m_\tau c} \frac{1}{2} \left(\vec{p}_\tau \vec{r}_\tau : \nabla_{\vec{R}} \mathring{\vec{A}}(\vec{R}) + \vec{r}_\tau \cdot \nabla_{\vec{R}} \mathring{\vec{A}}(\vec{R}) \cdot \vec{p}_\tau \right) \right.$$

$$\left. + \frac{1}{2} e_\tau \mathring{\phi}(\vec{R}) + \frac{1}{2} e_\tau \vec{r}_\tau \cdot \nabla_{\vec{R}} \mathring{\phi}(\vec{R}) + \frac{1}{4} e_\tau \vec{r}_\tau \vec{r}_\tau : \nabla_{\vec{R}} \nabla_{\vec{R}} \mathring{\phi}(\vec{R}) \right\} . \tag{20}$$

By use of the commutation rule

$$p_{\tau j} r_{\tau i} - r_{\tau i} p_{\tau j} = \frac{\hbar}{i} \delta_{ij} \ , \tag{21}$$

where the subscripts i and j now refer to components of the vectors along one or the other of three orthogonal unit vectors, it is immediately found that

$$\vec{r}_\tau \cdot \nabla_{\vec{R}} \mathring{\vec{A}}(\vec{R}) \cdot \vec{p}_\tau = \vec{p}_\tau \vec{r}_\tau : \nabla_{\vec{R}} \mathring{\vec{A}}(\vec{R}) - \frac{\hbar}{i} \nabla_{\vec{R}} \cdot \mathring{\vec{A}}(\vec{R}) . \tag{22}$$

Use of equation (22) and the self-adjoint character of the

operators $\vec{r}_\tau$ and $\vec{p}_\tau$ leads to the relation

$$\nabla_{\vec{R}} \vec{A}(\vec{R}) : \left[(\vec{p}_\tau \vec{r}_\tau)_{i\kappa} \vec{\mu}_{\kappa i} \right]^* = \vec{\mu}_{i\kappa} (\vec{p}_\tau \vec{r}_\tau)_{\kappa i} : \nabla_{\vec{R}} \vec{A}(\vec{R})$$

$$- \frac{\hbar}{i} \vec{\mu}_{i\kappa} \nabla_{\vec{R}} \cdot \vec{A}(\vec{R}) \delta_{i\kappa} \qquad (23)$$

Here the subscripts i and j denote the usual quantum mechanical matrix elements. The dipole moment operator of the molecule is given by

$$\vec{\mu} = \sum_\tau \vec{\mu}_\tau = \sum_\tau e_\tau \vec{r}_\tau \quad , \qquad (24)$$

and in the unperturbed representation, in which $\overset{o}{H}$ is diagonal, the relation

$$\sum_\tau \frac{e_\tau}{2 m_\tau c} (\vec{p}_\tau)_{i\kappa} = \frac{2\pi i \nu_{i\kappa} \vec{\mu}_{i\kappa}}{2c} \qquad (25)$$

is valid, the sums in equations (24) and (25) being over all particles of the molecule. It is convenient also to introduce the quadrupole moment tensor operator $\underline{Q} = \sum_\tau e_\tau \vec{r}_\tau \vec{r}_\tau$.

Substitution of equation (20) into (13) with use of equations (21 - 26), after a considerable amount of algebraic manipulation, gives the following expression for the moment induced by the electromagnetic field in the molecule, if the latter is originally in the quantum state specified

by the index i (which should be considered as representing a set of quantum numbers):

$$\vec{\mu}'_{ii} = \vec{E}\cdot\sum_{K}\frac{2\mathring{\nu}_{Ki}}{\hbar(\mathring{\nu}_{Ki}^2-\nu^2)}\,\mathrm{Re}\left[\mathring{\vec{\mu}}_{iK}\mathring{\vec{\mu}}_{Ki}\right] + \dot{\vec{E}}\cdot\sum_{K}\frac{\mathrm{Im}\left[\mathring{\vec{\mu}}_{iK}\mathring{\vec{\mu}}_{Ki}\right]}{\pi\hbar(\mathring{\nu}_{Ki}^2-\nu^2)}$$

$$+\nabla\vec{A}:\sum_{K}\frac{4\mathring{\nu}_{Ki}}{\hbar(\mathring{\nu}_{Ki}^2-\nu^2)}\,\mathrm{Re}\left[\mathring{\underline{\underline{\vartheta}}}_{iK}\mathring{\vec{\mu}}_{Ki}\right] + \nabla\dot{\vec{A}}:\sum_{K}\frac{2\,\mathrm{Im}\left[\mathring{\underline{\underline{\vartheta}}}_{iK}\mathring{\vec{\mu}}_{Ki}\right]}{\pi\hbar(\mathring{\nu}_{Ki}^2-\nu^2)}$$

$$-\frac{1}{2\pi^2\nu^2}(\nabla\cdot\dot{\vec{A}})\mathring{\vec{\mu}}_{ii}\sum_{T}\frac{e_T}{2m_Tc} - \nabla\nabla\phi:\sum_{K}\frac{\mathring{\nu}_{Ki}\,\mathrm{Re}\left[\mathring{\underline{\underline{Q}}}_{iK}\mathring{\vec{\mu}}_{Ki}\right]}{\hbar(\mathring{\nu}_{Ki}^2-\nu^2)}$$

$$-\nabla\nabla\dot{\phi}:\sum_{K}\frac{\mathrm{Im}\left[\mathring{\underline{\underline{Q}}}_{iK}\mathring{\vec{\mu}}_{Ki}\right]}{2\pi\hbar(\mathring{\nu}_{Ki}^2-\nu)}\quad,$$

$$\underline{\underline{\vartheta}} = \sum_{T}\frac{e_T}{2m_Tc}\,\vec{p}_T\vec{r}_T\quad.$$

(27)

In writing equation (27) we have omitted indicating explicitly the dependence of the fields on the position $\vec{R}$. The notations Re and Im indicate that the real and imaginary parts (respectively) of the quantity are to be taken. A dot over a quantity is used to denote differentiation with respect to time.

In the same way we calculate the induced magnetic moment in the quantum state specified by the index i, obtaining

$$\vec{m}'_{ii} = \vec{E}\cdot\sum_{\kappa}\frac{2\mathring{\nu}_{\kappa i}\,\mathrm{Re}[\mathring{\vec{\mu}}_{i\kappa}\mathring{\vec{m}}_{\kappa i}]}{h(\mathring{\nu}_{\kappa i}^2-\nu^2)} + \dot{\vec{E}}\cdot\sum_{\kappa}\frac{\mathrm{Im}[\mathring{\vec{\mu}}_{i\kappa}\mathring{\vec{m}}_{\kappa i}}{\pi h(\mathring{\nu}_{\kappa i}^2-\nu^2)}$$

$$+\nabla\vec{A}:\sum_{\kappa}\frac{4\mathring{\nu}_{\kappa i}\,\mathrm{Re}[\mathring{\underline{\vartheta}}_{i\kappa}\mathring{\vec{m}}_{\kappa i}]}{h(\mathring{\nu}_{\kappa i}^2-\nu^2)} + \nabla\dot{\vec{A}}:\sum_{\kappa}\frac{2\,\mathrm{Im}[\mathring{\underline{\vartheta}}_{i\kappa}\mathring{\vec{m}}_{\kappa i}]}{\pi h(\mathring{\nu}_{\kappa i}^2-\nu^2)}$$

$$-\frac{1}{2\pi^2\nu^2}(\nabla\cdot\dot{\vec{A}})\mathring{\vec{m}}_{ii}\sum_{\tau}\frac{e_\tau}{2m_\tau c} - \nabla\nabla\phi:\sum_{\kappa}\frac{\mathring{\nu}_{\kappa i}\,\mathrm{Re}[\mathring{\underline{Q}}_{i\kappa}\mathring{\vec{m}}_{\kappa i}]}{h(\mathring{\nu}_{\kappa i}^2-\nu^2)}$$

$$-\nabla\nabla\dot{\phi}:\sum_{\kappa}\frac{\mathrm{Im}[\mathring{\underline{Q}}_{i\kappa}\mathring{\vec{m}}_{\kappa i}]}{2\pi h(\mathring{\nu}_{\kappa i}^2-\nu^2)}\ .$$

(28)

Here $\vec{m}$ is the magnetic moment operator (neglecting spin) defined by

$$\vec{m} = \sum_{\tau}\frac{e_\tau}{2m_\tau c}\,\vec{r}_\tau\times\vec{p}_\tau\ .$$

Part II: Statistical mechanical theory

Equations (27) and (28) of Part I give the moments induced by a periodic electromagnetic field in a molecule originally (i.e., before the application of the electromagnetic field) in the quantum state specified by the index i.

For discussion of the macroscopic properties of the system it is convenient to introduce the macroscopic polarization $\vec{P}$. The instantaneous value $\vec{P}(\vec{r},t)$ of this quantity at the position $\vec{r}$ and time t is the sum of the moments of all the molecules which are in a fixed region ω about $\vec{r}$ at the time t, divided by the volume of the region ω. The dimensions of the region ω are to be small compared to the wave length of the radiation, but large enough to contain a large number of molecules. The observed polarization $\vec{P}$ is the statistical average of this value over the various states of the system of N molecules. This quantity may be taken as the product of the mean number of molecules per unit volume times the mean moment induced in a molecule fixed at the position $\vec{r}$, the mean being taken over all the states of the system consistent with the given molecule fixed at $\vec{r}$.

Proceeding in this fashion, we have to average expressions (27) and (28) in the fashion just mentioned. Inasmuch

as we intend to obtain expressions for the induced moments only to the first order in the field vectors, which already appear in (27) and (28), it will be appropriate to use the distribution functions valid for the unperturbed system. In our discussions of the averaging process we will continue to consider averages over quantum states as regards the internal degrees of freedom of the molecules, but rather than consider explicitly the quantum mechanical translational states, we will treat these classically. We suppose that the averaging over the translational degrees of freedom (i.e., the positions of the molecules of the system) and the averaging over the internal configurations (including the quantum states associated with the orientation and rotation of each molecule as a whole) may be carried out independently, as well as the averaging over internal quantum states of one molecule independently of that of the others. We allow intermolecular interactions of a type giving molecules their physical size, but neglect dependence of internal quantum states on the presence of other molecules. Stated otherwise, we suppose the internal quantum states of a given molecule (including the orientation of the molecule as a whole) to be independent of the states (i.e., position and internal quantum states) of the other molecules of the system.

We will consider the system composed of N molecules in internal quantum states i_r at position $\vec{r}_r$, r = 1, ...N.

An index i, without subscript, will be used to represent the set of indices i_r, r = 1....N. The vector potential at the position $\vec{r}_r$ of the rth molecule is given by

$$\vec{A}(\vec{r}_r, t)^{(i)} = \vec{A}^{(e)}(\vec{r}_r, t) + \sum_{\substack{s=1 \\ \neq r}}^{N} \vec{A}(\vec{r}_r, t ; \vec{r}_s)^{(i)}, \tag{29}$$

Where $\vec{A}^{(e)}(\vec{r}_r, t)$ is the vector potential at the position $\vec{r}_r$ and time t, due to external charge distributions and $\vec{A}(\vec{r}_r, t; \vec{r}_s)^{(i)}$ is the vector potential at position $\vec{r}_r$ and time t due to the induced moments in molecule s in quantum state i_s at position $\vec{r}_s$:

$$A(\vec{r}_r, t ; \vec{r}_s)^{(i)} = \frac{1}{c} \frac{[\dot{\vec{\mu}}_s^{(i)}]}{R_{rs}} + \nabla_r \times \frac{[\vec{m}_s^{(i)}]}{R_{rs}} . \tag{30}$$

Here $\vec{\mu}_s^{(i)}$ and $\vec{m}_s^{(i)}$ are, respectively, the electric and magnetic moments induced in molecule s in quantum state i_s and at position $\vec{r}_s$, and the square brackets mean that retardation is to be taken into account, i.e., the moments are to be taken at the time $t - \frac{R_{rs}}{c}$, where $\vec{R}_{rs} = \vec{r}_s - \vec{r}_r$, $R_{rs} = |\vec{R}_{rs}|$. Strictly speaking the positions vary with time, and R_{rs} should also be evaluated at the retarded time. We will neglect this however inasmuch as we may suppose the molecular velocities to be small compared to the velocity of light.

Similarly we find for the scalar potential the equations

$$\phi(\vec{r}_r,t)^{(i)} = \phi^{(e)}(\vec{r}_r,t) + \sum_{\substack{s=1 \\ \neq r}}^{N} \phi(\vec{r}_r,t;\vec{r}_s)^{(i)} , \tag{31}$$

$$\phi(\vec{r}_r,t;\vec{r}_s)^{(i)} = -\nabla_r \cdot \frac{[\vec{M}_s^{(i)}]}{R_{rs}} . \tag{32}$$

Equations (27 - 32) give a system of 2N equations for the determination of the electric and magnetic moments induced in each molecule for the system as specified by the internal quantum states and positions of each molecule. These could in principle be solved for the moments in terms of the externally imposed potentials, the geometry of the system, and the molecular parameters involved in (27) and (28). The resulting expressions might then be averaged over the internal quantum states and all positions of N-1 of the molecules relative to the Nth molecule considered fixed at a given position in order to arrive at the average electric and magnetic moments per molecule at the given position.

Rather than attempt this method we shall here proceed by a simpler path with the aid of certain approximations. Instead of solving the system of 2N equations just mentioned we immediately perform the averaging over internal quantum

states. A typical term on the right-hand side of the equation giving the induced moment in molecule r in quantum state i_r, at the position $\vec{r}_r$, the other molecules being in quantum states i_s, at the positions $\vec{r}_s$ (s =1,2....N, $s \neq r$), is $F(\vec{R}_{rs}, \vec{\mu}_s^{(i)}) \cdot \underset{\sim}{\alpha}^{i_r}$ where $F(\vec{R}_{rs}, \vec{\mu}_s^{(i)})$ is a field function (a vector or a tensor; for instance, the electric intensity) at the position $\vec{r}_r$ due to the moment $\vec{\mu}_s^{(i)}$ at $\vec{r}_s$, and $\underset{\sim}{\alpha}^{i_r}$ is a molecular tensor determined entirely by the quantum state i_r of molecule r. Indicating an average over internal quantum states of all molecules by a bar, the approximation which we will introduce is

$$\overline{F(\vec{R}_{rs}, \vec{\mu}_s^{(i)}) \cdot \underset{\sim}{\alpha}^{i_r}} \approx \overline{F(\vec{R}_{rs}, \vec{\mu}_s^{(i)})} \cdot \overline{\underset{\sim}{\alpha}^{i_r}} = F(\vec{R}_{rs}, \overline{\vec{\mu}_s^{(i)}}) \cdot \overline{\underset{\sim}{\alpha}^{i_r}} \qquad (33)$$

where the second step, an equality, is by virtue of the fact that in the field functions typified by F the only factors depending on the internal quantum states are the moments typified by $\vec{\mu}_s^{(i)}$.

According to our earlier assumptions, the internal quantum levels of each molecule will be degenerate, corresponding classically to no dependence of the energy of a molecule on its orientation. It is convenient for these reasons to introduce the über-matrix notation of Born, using a superscript index to represent the totality of quantum numbers except the degenerate orientational quantum number, and a subscript indicating the latter. Thus $\mathring{\mu}^{n'n}_{m'm}$

is the matrix element of the dipole moment between the unperturbed state specified by the quantum index n' and the quantum number m' and the state specified by n and m. The notation $\mathring{\vec{\mu}}^{n'n}$ represents the rectangular matrix ($\mathring{\vec{\mu}}^{n'n}_{m'm}$) of $g_{n'}$ columns and g_n rows, obtained from the set of all quantum numbers m' and m existing for the states specified by the indices n' and n, respectively, where g_n is the degree of orientational degeneracy. We will use the usual abbreviation $\mathrm{Sp}\, A^{nn} = \sum_m A^{nn}_{mm}$, where the sum is over the orientational substates of state n and A is any matrix. As is well known, such a quantity is a rotational invariant, which is to say that the quantity does not depend on the choice of the axis of quantization of the total angular momentum. The energy of the unperturbed quantum states we denote by $\mathring{W}^{(n)}$, an orientational index being superfluous because of the assumed degeneracy. The quantum statistical weight factors are $e^{-\frac{\mathring{W}^{(n)}}{kT}}$, here k being Boltzmann's constant, T the absolute temperature.

In the new notation, and with the approximation of replacing the average over internal quantum states of the product of two functions by the product of their averages, the moment in molecule r fixed at $\vec{r}_r$ averaged over internal quantum states, but with the other molecules in fixed positions, is

$$\overline{\vec{\mu}^{(r)}} = \sum_{n_r} \frac{B_r}{g_{n_r}} Sp\left[\mathring{\vec{\mu}}_r^{n_r n_r}\right] e^{-\frac{\mathring{w}^{n_r}}{KT}} +$$

$$\vec{E}_r \cdot \sum_{n_r} \frac{B_r}{g_{n_r}} \left(\sum_{n_r'} \frac{2\mathring{\nu}^{n_r' n_r}}{h(\mathring{\nu}^{n_r' n_r} n_r^2 - \nu^2)} Re\left\{ Sp\left[\mathring{\vec{\mu}}_r^{n_r n_r'} \mathring{\vec{\mu}}_r^{n_r' n_r}\right]\right\}\right) e^{-\frac{\mathring{w}^{n_r}}{KT}}$$

$$+ \dot{\vec{E}}_r \cdot \sum_{n_r} \frac{B_r}{g_{n_r}} \left(\sum_{n_r'} \frac{Im\left\{ Sp\left[\mathring{\vec{\mu}}_r^{n_r n_r'} \mathring{\vec{\mu}}_r^{n_r' n_r}\right]\right\}}{\pi h(\mathring{\nu}^{n_r' n_r^2} - \nu^2)}\right) e^{-\frac{\mathring{w}^{n_r}}{KT}}$$

$$+ \nabla \vec{A}_r : \sum_{n_r} \frac{B_r}{g_{n_r}} \left(\sum_{n_r'} \frac{4\mathring{\nu}^{n_r' n_r} Re\left\{ Sp\left[\mathring{\underset{\sim}{\vartheta}}_r^{n_r n_r'} \mathring{\vec{\mu}}_r^{n_r' n_r}\right]\right\}}{\pi h(\mathring{\nu}^{n_r' n_r^2} - \nu^2)}\right) e^{-\frac{\mathring{w}^{n_r}}{KT}}$$

$$+ \nabla \dot{\vec{A}}_r : \sum_{n_r} \frac{B_r}{g_{n_r}} \left(\sum_{n_r'} \frac{2\, Im\left\{ Sp\left[\mathring{\underset{\sim}{\vartheta}}_r^{n_r n_r'} \mathring{\vec{\mu}}_r^{n_r' n_r}\right]\right\}}{\pi h(\mathring{\nu}^{n_r' n_r^2} - \nu^2)}\right) e^{-\frac{\mathring{w}^{n_r}}{KT}}$$

$$- \frac{1}{2\pi^2 \nu^2} (\nabla \cdot \vec{A}_r) \left(\sum_{\tau} \frac{e_\tau}{2 m_\tau C}\right) \sum_{n_r} \frac{B_r}{g_{n_r}} Sp\left[\mathring{\vec{\mu}}_r^{n_r n_r}\right] e^{-\frac{\mathring{w}^{n_r}}{KT}}$$

$$- \nabla\nabla \phi_r : \sum_{n_r} \frac{B_r}{g_{n_r}} \left(\sum_{n_r'} \frac{\mathring{\nu}^{n_r' n_r} Re\left\{ Sp\left[\mathring{\underset{\sim\sim}{Q}}_r^{n_r n_r'} \mathring{\vec{\mu}}_r^{n_r' n_r}\right]\right\}}{h(\mathring{\nu}^{n_r' n_r^2} - \nu^2)}\right) e^{-\frac{\mathring{w}^{n_r}}{KT}}$$

$$- \nabla\nabla \dot{\phi}_r : \sum_{n_r} \frac{B_r}{g_{n_r}} \left(\sum_{n_r'} \frac{Im\left\{ Sp\left[\mathring{\underset{\sim\sim}{Q}}_r^{n_r n_r'} \mathring{\vec{\mu}}_r^{n_r' n_r}\right]\right\}}{2\pi h(\mathring{\nu}^{n_r' n_r^2} - \nu^2)}\right) e^{-\frac{\mathring{w}^{n_r}}{KT}} \quad ;$$

$$B_r = \frac{1}{\sum_{n_r} e^{-\frac{\mathring{w}^{n_r}}{KT}}} \quad .$$

(34)

A similar formula holds for $\vec{m}^{(r)}$. Here, in using equations (29 - 32) for the field vectors, the unaveraged moments there appearing are to be replaced by the averaged moments, in accordance with the approximation of equation (33). The rotational invariance of the spurs in equation (34) results in a far-reaching simplification. In a freely rotatable system, to which class these zero-order spurs belong under our assumptions, the following relations hold[23]:

$$Sp[A^{nn}_i] = 0 \quad , \tag{35}$$

$$Sp[A^{nn'}_i B^{n'n}_j] = \delta_{ij} \frac{1}{3} Sp[\vec{A}^{nn'} \cdot \vec{B}^{n'n}], \tag{36}$$

$$Sp[T^{nn'}_{ij} A^{n'n}_k] = \delta_{ijk} Sp[T^{nn'}_{12} A^{n'n}_3] \ . \tag{37}$$

$\vec{A}$ and $\vec{B}$ are vectors with constant components with respect to a set of axes fixed in the molecule, and $\underline{\underline{T}}$ is a tensor with constant elements with respect to the same axes. If $\vec{e}_1$, $\vec{e}_2$, $\vec{e}_3$ are a given triad of orthogonal unit vectors fixed in space, the A_i is defined by $A_i = \vec{A} \cdot \vec{e}_i$, i = 1,2,3, and T_{ij} in dyadic notation by $T_{ij} = \vec{e}_i \cdot \underline{\underline{T}} \cdot \vec{e}_j$, i, j = 1,2,3. δ_{ij} is the usual Kronecker delta symbol; δ_{ijk}, i, j, k = 1,2,3, is the alternating symbol, defined as equal to zero unless the indices i, j, and k are all different, and as equal to plus or minus one according as the sequence i j k is an even or odd permutation of the sequence 1 2 3.

Considering now the terms on the right-hand side of equation (34), the first and sixth evidently vanish by virtue of equation (35). The second and third terms each contain a factor of the form $\vec{E}_r \cdot \mathrm{Sp}\left[\mathring{\mu}_r^{n_r n_r'} \mathring{\mu}_r^{n_r' n_r}\right]$, which can evidently be written $\vec{E}_r \, \mathrm{Sp}\left[\mathring{\mu}_r^{n_r n_r'} \cdot \mathring{\mu}_r^{n_r' n_r}\right]$. The spur in this is evidently real, so that the Re in the second term may be omitted, while the third term vanishes. The fourth and fifth terms each contain a factor of the form $\nabla \vec{A}_r : \mathrm{Sp}\left[\underline{\underline{\mathring{\vartheta}}}_r^{n_r n_r'} \mathring{\mu}_r^{n_r' n_r}\right]$, which may be written, temporarily dropping the molecule-identifying subscripts and adopting a coordinate notation,

$$\sum_{i,j,K=1}^{3} \vec{e}_K \frac{\partial A_i}{\partial X_j} \mathrm{Sp}\left[\mathring{\vartheta}_{ij}^{nn'} \mathring{\mu}_K^{n'n}\right] ,$$

where the X_j, $j = 1, 2, 3$ are the components of $\vec{R}$ in the notation of equations (35-37), and similarly for the A_i. From (37) one obtains immediately

$$\mathrm{Sp}\left[T_{ij} A_K\right] = - \mathrm{Sp}\left[T_{ji} A_K\right] . \tag{38}$$

Using this, we may write the preceding expression as

$$\tfrac{1}{2} \sum_{K=1}^{3} \vec{e}_K \left(\frac{\partial A_i}{\partial X_j} - \frac{\partial A_j}{\partial X_i} \right) \mathrm{Sp}\left[\left(\mathring{\vartheta}_{ij}^{nn'} - \mathring{\vartheta}_{ji}^{nn'} \right) \mathring{\mu}_K^{n'n} \right] ,$$

where i and j are the two indices different from k. We note that the components of the magnetic moment may be expressed as

$$m_x = \vartheta_{zy} - \vartheta_{yz} \quad , \text{etc.} \tag{39}$$

Thus we may finally write the factor in the fourth term, using equation (36) and returning to vector notation in the form $1/6\ (\nabla \times \vec{A})\ \mathrm{Sp}[\vec{m}^{nn'} \cdot \vec{\mu}^{n'n}]$. If we notice that the dyad $\underline{\underline{Q}}$ appearing in the seventh and eighth terms is symmetric, we see that these terms vanish by virtue of equation (38). Thus equation (34) simplifies to

$$\overline{\vec{\mu}^{(r)}} = \alpha \vec{E}_r + \beta \vec{B}_r - \gamma \dot{\vec{B}}_r \quad , \tag{40}$$

while a similar procedure gives

$$\overline{\vec{m}^{(r)}} = \beta \vec{E} + \gamma \dot{\vec{E}} + \mu \vec{B}_r \quad , \tag{41}$$

where

$$\alpha = \sum_n \left(\frac{2B}{3\hbar g_n} \sum_{n'} \frac{\mathring{\nu}^{n'n}\, \mathrm{Sp}[\mathring{\vec{\mu}}^{nn'} \cdot \mathring{\vec{\mu}}^{n'n}]}{\mathring{\nu}^{n'n^2} - \nu^2} \right) e^{-\frac{\mathring{W}^n}{KT}} \quad , \tag{42}$$

$$\beta = \sum_n \left(\frac{2B}{3\hbar g_n} \sum_{n'} \frac{\mathring{\nu}^{n'n}\, \mathrm{Re}\{\mathrm{Sp}[\mathring{\vec{\mu}}^{nn'} \cdot \mathring{\vec{m}}^{n'n}]\}}{\mathring{\nu}^{n'n^2} - \nu^2} \right) e^{-\frac{\mathring{W}^n}{KT}} \quad , \tag{43}$$

$$\gamma = \sum_n \left(\frac{B}{3\pi\hbar g_n} \sum_{n'} \frac{\mathrm{Im}\{\mathrm{Sp}[\mathring{\vec{\mu}}^{nn'} \cdot \mathring{\vec{m}}^{n'n}]\}}{\mathring{\nu}^{n'n^2} - \nu^2} \right) e^{-\frac{\mathring{W}^n}{KT}} \quad , \tag{44}$$

$$\mu = \sum_n \left(\frac{2B}{3h g_n} \sum_{n'} \frac{\nu_{n'n} \, Sp[\dot{\vec{m}}^{nn'} \cdot \dot{\vec{m}}^{n'n}]}{\nu_{n'n}^2 - \nu^2} \right) e^{-\frac{\dot{W}^n}{KT}} \tag{45}$$

$$B = \frac{1}{\sum_n e^{-\frac{\dot{W}^n}{KT}}} \tag{46}$$

In equations (42 - 46) we have omitted the molecule-identifying subscripts, since we are supposing the system to consist of a single variety of molecules.

For the majority of substances of interest in a discussion of optical activity, μ is very small. Since, moreover, it does not contribute to the optical activity, we will therefore omit it from further discussion so as not to unduly complicate our formulas. The quantities β and γ are also small, but the latter will be shown to be the term responsible for the optical activity, and so cannot be neglected. We will retain β in order to show that it does not contribute to the optical activity. The field vectors in (40) and (41) depend on the positions of all the molecules, and we must still average these expressions over the positions of the molecules.

In the following we will use the complex representation

of the fixed vectors and moments, in which

$$\vec{E}_r = \vec{E}(\vec{r}_r, t) = \vec{E}^{\circ}(\vec{r}_r)\, e^{-i\omega t}, \text{ etc.},$$

$$\omega = 2\pi\nu \tag{47}$$

where $\vec{r}_r$ is the vector position of the center of gravity of molecule r with respect to any convenient origin. Dependence on the positions of the other molecules is still to be understood.

Using equation (47) and the following one of Maxwell's equations,

$$\nabla \times \vec{E} = -\frac{1}{c}\dot{\vec{B}} \ , \tag{48}$$

equations (40) and (41) may be written in abbreviated form

$$\vec{\mu}_i = \alpha \vec{E}_i + \frac{c}{i\omega}(\beta + i\omega\gamma)\nabla_i \times \vec{E}_i \tag{49}$$

$$\vec{m}_i = (\beta - i\omega\gamma)\vec{E}_i \tag{50}$$

where we have changed the index designating the various molecules to avoid confusion with the molecular coordinates, and use it now as a subscript rather than superscript. The explicit dependence of $\vec{E}_i$ on $\vec{E}^{(e)}$ and the induced moments and positions of the other molecules may be written, using

equations (29 - 32)

$$\vec{E}(\vec{r}_i,t) = \vec{E}^{(e)}(r_i,t) + \sum_{\substack{J=1 \\ \neq i}}^{N} \mathrm{curl}_i\,\mathrm{curl}_i \frac{[\vec{\mu}_j]}{R_{ij}} - \frac{1}{c}\sum_{\substack{J=1 \\ \neq i}}^{N} \mathrm{curl}_i \frac{[\dot{\vec{m}}_j]}{R_{ij}} \quad , \tag{51}$$

$$\vec{R}_{ij} = \vec{r}_j - \vec{r}_i \quad ; \quad R_{ij} = |\vec{R}_{ij}| \, . \tag{52}$$

Substituting equation (51) into equations (49) and (50) and indicating the spatial averaging by a second bar, we obtain the equations

$$\overline{\vec{\mu}_i} = \alpha \vec{E}_i^{(e)} + \frac{c}{i\omega}(\beta + i\omega\gamma)\,\mathrm{curl}_i \vec{E}_i^{(e)} + \alpha \sum_{\substack{J=1 \\ \neq i}}^{N} \overline{\mathrm{curl}_i\,\mathrm{curl}_i \frac{[\vec{\mu}_j]}{R_{ij}}} + \frac{c}{i\omega}(\beta + i\omega\gamma) \sum_{\substack{J=1 \\ \neq i}}^{N} \overline{\mathrm{curl}_i\,\mathrm{curl}_i\,\mathrm{curl}_i \frac{[\vec{\mu}_j]}{R_{ij}}} - \frac{\alpha}{c} \sum_{\substack{J=1 \\ \neq i}}^{N} \overline{\mathrm{curl}_i \frac{[\dot{\vec{m}}_j]}{R_{ij}}} \, , \tag{53}$$

$$\overline{\vec{m}_i} = (\beta - i\omega\gamma)\vec{E}_i^{(e)} + (\beta - i\omega\gamma) \sum_{\substack{J=1 \\ \neq i}}^{N} \overline{\mathrm{curl}_i\,\mathrm{curl}_i \frac{[\vec{\mu}_j]}{R_{ij}}} \quad . \tag{54}$$

The averaging indicated by the second bar is to be done with molecule i considered fixed in space at the position $\vec{r}_i$, all spatial configurations of the other molecules being weighted appropriately. In both (53) and (54) a term in which $(\beta \pm i\omega\gamma)$ multiplies an expression containing the

magnetic moment has been omitted since inspection of (50) shows that such a term is of second order in the retarded quantities β and γ . The latter are small, and furthermore we have throughout the discussion considered only first order retarded terms. In (51) and (52) we have neglected the contributions of quadrupole and higher multipole moments to the electric intensity.

In solving (53) and (54) for the average induced moments we will follow a procedure similar to Born's[24] account of the "Oseen process"[12](see also (20)) for the case in which the terms in β and γ are absent. Implicit in the method, but not explicitly stated by him, is a further approximation similar to the one used earlier to simplify equations (27) and (28). We approximate $\overline{\text{curl}_i \text{ curl}_i \frac{1}{R_{ij}}[\vec{\mu}_j]}$ by $\overline{\text{curl}_i \text{ curl}_i \frac{1}{R_{ij}}[\vec{\vec{\mu}}_j]}$ and similarly for the other averages. This evidently involves neglecting certain translational fluctuations. The functional dependence of $\vec{\vec{\mu}}_j$ and $\vec{\vec{\mu}}_i$ on the positions $\vec{r}_j$ and $\vec{r}_i$ and on the time is now evidently the same, and further there is evidently now no distinction between the molecules previously designated by the index j. To simplify writing we will now drop the double bars; we will further discontinue the use of the subscripts to designate the various molecules, and use instead $\vec{\mu}(\vec{r},t)$ to denote the average moment in a molecule fixed at $\vec{r}$, and $\vec{\mu}(\vec{r}',t)$ to denote the average moment in a molecule at $\vec{r}'$. The averaging process referred

to is that previously denoted by the double bar. The operations curl, grad, etc., (or∇) without any identification will refer to vector differentiation with respect to $\vec{r}$; where there is occasion to use vector differentiation with respect to $\vec{r}'$, the notations curl', grad', etc., (or∇) will be used. We obtain in place of equations (53) and (54)

$$\vec{\mu}(\vec{r},t) = \alpha \vec{E}^{(e)}(\vec{r},t) + \frac{c}{i\omega}(\beta + i\omega\gamma)\,\mathrm{curl}\,\vec{E}^{(e)}(\vec{r},t) + N\alpha\,\overline{\mathrm{curl}\,\mathrm{curl}\,\frac{[\vec{\mu}(\vec{r}',t)]}{R}}$$

$$+ \frac{cN(\beta+i\omega\gamma)}{i\omega}\,\overline{\mathrm{curl}\,\mathrm{curl}\,\mathrm{curl}\,\frac{[\vec{\mu}(\vec{r}',t)]}{R}} - \frac{N\alpha}{c}\,\overline{\mathrm{curl}\,\frac{[\dot{\vec{m}}(\vec{r}',t)]}{R}}\ , \tag{55}$$

$$\vec{m}(\vec{r},t) = (\beta - i\omega t)\vec{E}^{(e)}(\vec{r},t) + N(\beta - i\omega\gamma)\,\overline{\mathrm{curl}\,\mathrm{curl}\,\frac{[\vec{\mu}(\vec{r}',t)]}{R}}\ , \tag{56}$$

$$\vec{R} = \vec{r} - \vec{r}'\ ,\quad R = |\vec{R}|\ . \tag{57}$$

The next step in the "Oseen process" is the introduction of the experimentally observed form of $\vec{\mu}(r',t)$,

$$\vec{\mu}(\vec{r}',t) = \vec{U}(\vec{r}')\,e^{-i\omega t}$$

$$\vec{U}(\vec{r}') = \vec{U}^{\circ} e^{i\frac{n\omega}{c}\vec{s}\cdot\vec{r}'} \tag{58}$$

$$\nabla' \cdot \vec{\mu}(\vec{r}',t) = 0$$

corresponding to the propagation of a plane wave through the system in the direction of the unit vector s with velocity c/n. $\vec{U}^{\circ}$ is a constant (complex) vector. Actually, experiment gives the average polarization. In our approximation the polarization and the average moment per molecule have the same functional dependence.

The assumption previously made, that the averaging over internal quantum states could be performed independently of the averaging over intermolecular distances, permits the pair distribution function for the latter to depend only on the magnitude of the distance. Therefore we introduce the radial distribution function g(R), such that $g(R)/V d\tau'$ is the probability of finding one member of a given pair in the volume element $d\tau'$ at position $\vec{r}'$ if the other is at $\vec{r}$. The normalization condition is

$$\frac{1}{V}\int_V g(R)\,d\tau' = 1 \quad , \tag{59}$$

where the integral is with respect to $\vec{r}'$, and extends over the space occupied by the system, the volume of the latter being denoted by V. The mean value $f(\vec{r})$ of a function $F(\vec{r},\vec{r}')$ for fixed $\vec{r}$ and variable $\vec{r}'$ is then given by

$$f(\vec{r}) = \frac{1}{V}\int_V F(\vec{r},\vec{r}')\, g(R)\,d\tau' \quad . \tag{60}$$

For a system of noninteracting mass points $g(R) = 1$. For a system of hard spheres of diameter a, $g(R) = 0$, $R<a$ while for $R>a$ a series of peaks and troughs of decreasing amplitude is obtained[25], with $g(R)\to 1$ as $R\to\infty$. The latter boundary condition is a general one for fluid systems. Indeed, in order for the normalization integral to converge, we must have $\lim_{R\to\infty} R^3 (g(R)-1) = 0$.

In general $g(R)$ will vanish within a region Ω in the neighborhood of $R = 0$ due to the short range intermolecular repulsive forces which give molecules their effective size. In our discussion we will suppose Ω to be sufficiently well-approximated by a sphere, the radius of which we will take to be a. Indicating the omission of the sphere Ω from the region of integration, and using the identity $g(R) = 1-(1-g(R))$, equation (60) may be written

$$f(\vec{r}) = \frac{1}{V}\int_{V-\Omega} F(\vec{r},\vec{r}')\,d\tau' - \frac{1}{V}\int_{V-\Omega} F(\vec{r},\vec{r}')(1-g(R))\,d\tau' \tag{61}$$

The first of the integrals in (61) is of the type considered by Born[24]; the second is related to the integral determining the scattering of x-rays by fluids.

The first of the averages in (55) may then be written, using (58) and (61), as

$$\overline{\operatorname{curl}\operatorname{curl}\frac{[\vec{\mu}(\vec{r}',t)]}{R}} = \frac{1}{V}\int_{V-\Omega}\operatorname{curl}\operatorname{curl}\left(\vec{U}(\vec{r}')\frac{e^{-i\omega(t-\frac{R}{c})}}{R}\right)d\tau'$$
$$-\frac{1}{V}\int_{V-\Omega}\operatorname{curl}\operatorname{curl}\left(\vec{U}(\vec{r}')\frac{e^{-i\omega(t-\frac{R}{c})}}{R}\right)(1-g(R))\,d\tau' \tag{62}$$

If we define

$$\varphi(R) = \frac{e^{\frac{i\omega R}{c}}}{R} \quad , \tag{63}$$

note that

$$\nabla'^2 \varphi(R) = -\frac{\omega^2}{c^2}\varphi(R) \quad , \tag{64}$$

and from (58) that

$$\nabla'^2 \vec{U}(\vec{r}') = -\frac{n^2\omega^2}{c^2}\vec{U}(\vec{r}') \tag{65}$$

we may write for the first integral of (62)

$$\int_{V-\Omega} \operatorname{curl}\operatorname{curl}\left(\vec{U}(\vec{r}')\frac{e^{-i\omega(t-\frac{R}{c})}}{R}\right)d\tau' =$$

$$\frac{c^2 e^{-i\omega t}}{\omega^2(n^2-1)}\int_{V-\Omega}\operatorname{curl}\operatorname{curl}\left(\vec{U}(\vec{r}')\nabla'^2\varphi(R) - \varphi(R)\nabla'^2\vec{U}(\vec{r}')\right)d\tau' =$$

$$\frac{c^2 e^{-i\omega t}}{\omega^2(n^2-1)}\int_{S_{V-\Omega}}\operatorname{curl}\operatorname{curl}\{\{\vec{U},\varphi\}\}\,d\sigma' \quad ,$$

(66)

where we have introduced the notation

$$\{\{\vec{U},\varphi\}\} = \vec{U}(\vec{r}')\frac{\partial\varphi(R)}{\partial\nu'} - \varphi(R)\frac{\partial\vec{U}(\vec{r}')}{\partial\nu'} \quad .$$

Green's theorem has been used to obtain the second equality, the integral now being over $\vec{r}'$ on the surface $S_{V-\Omega}$ of the region $V-\Omega$, $\frac{\partial}{\partial \nu'}$ indicating the directional derivative along the outward-drawn normal.

This last integral may be written as the sum of an integral over the external surface Σ of V and an integral over the surface σ of the sphere Ω. Reversing the sign of the latter integral so that the notation $\frac{\partial}{\partial \nu'}$ may uniformly mean the derivative along the outward-drawn normal to the surface of integration, equation (66) may be written

$$\int_{V-\Omega} \text{curl}\,\text{curl}\,\frac{\vec{U}(\vec{r}')\,e^{-i\omega\left(t-\frac{R}{c}\right)}}{R}\,d\tau' = \vec{I}_1 + \vec{I}_2 \tag{67}$$

$$\vec{I}_1 = \frac{-c^2 e^{-i\omega t}}{\omega^2(n^2-1)} \int_{\sigma} \text{curl}\,\text{curl}\,\{\{\vec{U}, \varphi\}\}\,d\sigma' \tag{68}$$

$$\vec{I}_2 = \frac{c^2 e^{-i\omega t}}{\omega^2(n^2-1)} \int_{\Sigma} \text{curl}\,\text{curl}\,\{\{\vec{U}, \varphi\}\}\,d\sigma' \tag{69}$$

It will be convenient for the sake of completeness to carry out here the evaluation of $\vec{I}_1$ as given by Born[24]. Performing the vector differentiations we have

$$I_1 = \frac{c^2 e^{-i\omega t}}{\omega^2 (n^2-1)} \int_\sigma \left\{ \left(\frac{\omega^2}{c^2} \varphi(R) - \frac{\varphi'(R)}{R} \right) \frac{\partial \vec{U}(\vec{r}')}{\partial R} + \frac{1}{R} \left(\frac{\varphi'(R)}{R} \right)' \vec{R}\,\vec{R} \cdot \frac{\partial \vec{U}(\vec{r}')}{\partial R} \right\} d\sigma'$$

$$- \frac{c^2 e^{-i\omega t}}{\omega^2 (n^2-1)} \int_\sigma \left\{ \left(\frac{\omega^2}{c^2} \varphi(R) + \frac{\varphi'(R)}{R} \right)' \vec{U}(\vec{r}') \cdot \left(\frac{1}{R} \left(\frac{\varphi'(R)}{R} \right)' \vec{R}\,\vec{R} \right)' \right\} d\sigma' , \tag{70}$$

where the primes mean differentiation with respect to the indicated argument of the function. With the notation

$$\vec{e} = \frac{\vec{R}}{R} , \tag{71}$$

$$\phi(R) = \frac{\varphi'(R)}{R} + \frac{\omega^2}{c^2} \varphi(R) , \tag{72}$$

$$\psi(R) = R \left(\frac{\varphi'(R)}{R} \right)' , \tag{73}$$

$$A = -4\pi a^2 \phi(a) , \tag{74}$$

$$B = -4\pi a^2 \psi(a) , \tag{75}$$

$$A' = -4\pi a^2 \phi'(a) , \tag{76}$$

$$B' = -4\pi a^2 \psi'(a) , \tag{77}$$

equation (70) may be written

$$\vec{I}_1 = \frac{c^2 e^{-i\omega t}}{\omega^2 (n^2-1)} \left\{ -A \overline{\left(\frac{\partial \vec{U}(\vec{r}')}{\partial R} \right)_{R=a}} - B \overline{\vec{e}\,\vec{e} \cdot \left(\frac{\partial \vec{U}(\vec{r}')}{\partial R} \right)_{R=a}} \right.$$

$$\left. + A' \left(\vec{U}(\vec{r}') \right)_{R=a} + B' \overline{\vec{e}\,\vec{e} \cdot \left(\vec{U}(\vec{r}') \right)_{R=a}} \right\} , \tag{78}$$

where the bars indicate averages over all directions of $\vec{e}$.

Expansion of $\vec{U}(r')$ and $\varphi(R)$ in powers of R, leads after performing the averaging indicated in equation (78), with use of the third of equations (58), to the relation

$$\vec{I}_1 = \frac{4\pi}{3}\,\frac{n^2+2}{n^2-1}\,\vec{\mu}(\vec{r},t) - \frac{16\pi^3}{3}\,\frac{n^2+10}{10}\left(\frac{a}{\lambda_0}\right)^2\vec{\mu}(\vec{r},t) + O\left(\frac{a^4}{\lambda_0^4}\right), \tag{79}$$

where λ_0 is the vacuum wave length. Since a is of the order of 10 Å, the second and following terms will be negligible for visible light ($\lambda_0 \approx 5000$Å). Equation (79) is that obtained by Born[24] except he did not compute the $\left(\frac{a}{\lambda_0}\right)^2$ term.

The second of the integrals in equation (62) may be approximated as follows. The factor (1 - g(R)) in the integrand is non-vanishing only for small R, so that the integral may be taken over the region between the surface R = a and some larger spherical surface R = b beyond which there is effectively no contribution to the integral; i.e.,

$$\int_{V-\Omega}\left(\text{curl curl}\,\frac{\vec{U}(\vec{r}')\,e^{-i\omega\left(t-\frac{R}{c}\right)}}{R}\right)\left(1-g(R)\right)d\tau' = \int_{a\le R\le b}\left(\text{curl curl}\,\frac{\vec{U}(\vec{r}')\,e^{-i\omega\left(t-\frac{R}{c}\right)}}{R}\right)\left(1-g(R)\right)d\tau'$$

$$= \sum_{i=0}^{L}\int_{R_i\le R\le R_i+\Delta R}\left(\text{curl curl}\,\frac{\vec{U}(\vec{r}')\,e^{-i\omega\left(t-\frac{R}{c}\right)}}{R}\right)\left(1-g(R)\right)d\tau', \tag{80}$$

where

$$R_0 = a\,,$$

$$R_{L+1} = b\,,$$

$$\Delta R = \frac{b-a}{L}\,. \tag{81}$$

We approximate $1 - g(R)$ in the interval $R_i \leq R < R_i + \Delta R$ by $(1 - g(R_i))$, and take this factor outside the integral. The integrand is then the same as that in the first of the integrals in (62), and may be transformed in the same way to surface integrals over the spherical surfaces $R = R_i$ and $R = R_i + \Delta R$. These may be evaluated using equation (79) providing that $\left(\frac{b}{\lambda_0}\right)^2 \ll 1$. In this way we find

$$\int_{V-\Omega} \left(\text{curl curl } \frac{\vec{U}(\vec{r}\,') e^{-i\omega(t-\frac{R}{c})}}{R}\right)(1 - g(R))\, d\tau' =$$

$$\frac{32\pi^3}{3} \frac{n^2+10}{10} \vec{\mu}(\vec{r}, t) \frac{1}{\lambda_0^2} \sum_{i=0}^{L} (1 - g(R_i)) R_i \Delta R + O\left(\frac{b}{\lambda_0}\right)^4 ,$$

(82)

which for large L becomes

$$\int_{V-\Omega} \left(\text{curl curl } \frac{\vec{U}(\vec{r}\,') e^{-i\omega(t-\frac{R}{c})}}{R}\right)(1 - g(R))\, d\tau' =$$

$$\frac{32\pi^3}{3} \frac{n^2+10}{10} \vec{\mu}(\vec{r}, t) \frac{1}{\lambda_0^2} \int_0^{\infty} (1 - g(R)) R\, dR + O\left(\frac{b}{\lambda_0}\right)^4 .$$

(83)

This term is of the order of $\left(\frac{b}{\lambda_0}\right)^2$, and for visible light may be supposed negligible.

Using equations (67, 79 and 83) in (62), we obtain

$$\overline{\operatorname{curl}\operatorname{curl}\frac{[\vec{\mu}(\vec{r}',t)]}{R}} = \frac{4\pi}{3V}\frac{n^2+2}{n^2-1}\vec{\mu}(\vec{r},t) + \frac{c^2}{\omega^2 V(n^2-1)}\int_{\Sigma}\operatorname{curl}\operatorname{curl}\{\{\vec{\mu},\varphi\}\}\,d\sigma' + O\left(\frac{b}{\lambda_0}\right)^2 .$$

(84)

The second of the averages in (55) may be written

$$\overline{\operatorname{curl}\operatorname{curl}\operatorname{curl}\frac{[\vec{\mu}(\vec{r}',t)]}{R}} = -\frac{\omega^2}{c^2}\frac{e^{-i\omega t}}{V}\int_{V-\Omega}\operatorname{curl}\left(\vec{U}(\vec{r}')\varphi(R)\right)d\tau' + \frac{\omega^2 e^{-i\omega t}}{c^2 V}\int_{V-\Omega}(\operatorname{curl}\vec{U}(\vec{r}')\,\varphi(R))(1-g(R))\,d\tau' .$$

(85)

A calculation similar to the foregoing gives

$$\overline{\operatorname{curl}\operatorname{curl}\operatorname{curl}\frac{[\vec{\mu}(\vec{r}',t)]}{R}} = \frac{4\pi}{V(n^2-1)}\nabla\times\vec{\mu}(\vec{r},t) - \frac{1}{V(n^2-1)}\int_{\Sigma}\operatorname{curl}\{\{\vec{\mu},\varphi\}\}\,d\sigma' + O\left(\frac{b}{\lambda_0}\right)^2$$

(86)

Again in the same way one finds

$$\frac{1}{c}\,\overline{\operatorname{curl}\frac{[\dot{\vec{m}}(\vec{r}';t)]}{R}} = \frac{c}{i\omega}\,\frac{4\pi}{V(n^2-1)}\,\nabla\times\vec{m}(\vec{r},t) + \frac{c}{i\omega}\,\frac{1}{V(n^2-1)}\int_\Sigma \operatorname{curl}\{\{\vec{m},\varphi\}\}\,d\sigma' + O\left(\frac{b}{\lambda_0}\right)^2. \tag{87}$$

Using (84 - 87), equations (55) and (56) may be written

$$\vec{\mu}(\vec{r},t) = \alpha\vec{E}^{(e)}(\vec{r},t) + \frac{c}{i\omega}(\beta+i\omega\gamma)\nabla\times\vec{E}^{(e)}(\vec{r},t) +$$

$$\frac{4\pi\bar{N}\alpha}{3}\,\frac{n^2+2}{n^2-1}\,\vec{\mu}(\vec{r},t) + \frac{c}{i\omega}\,\frac{4\pi\bar{N}(\beta+i\omega\gamma)}{n^2-1}\,\nabla\times\vec{\mu}(\vec{r},t) -$$

$$\frac{c}{i\omega}\,\frac{4\pi\bar{N}\alpha}{n^2-1}\,\nabla\times\vec{m}(\vec{r},t) + \frac{c^2\bar{N}\alpha}{\omega^2(n^2-1)}\int_\Sigma \operatorname{curl}\operatorname{curl}\{\{\vec{\mu},\varphi\}\}\,d\sigma'$$

$$+ \frac{c^3}{i\omega^3}\,\frac{\bar{N}(\beta+i\omega\gamma)}{n^2-1}\int_\Sigma \operatorname{curl}\operatorname{curl}\operatorname{curl}\{\{\vec{\mu},\varphi\}\}\,d\sigma' -$$

$$\frac{c}{i\omega}\,\frac{\bar{N}\alpha}{n^2-1}\int_\Sigma \operatorname{curl}\{\{\vec{m},\varphi\}\}\,d\sigma' + O\left(\frac{b}{\lambda_0}\right)^2 \quad ; \tag{88}$$

$$\vec{m}(\vec{r},t) = (\beta-i\omega\gamma)\vec{E}^{(e)}(\vec{r},t) + \frac{4\pi\bar{N}(\beta-i\omega\gamma)}{3}\,\frac{n^2+2}{n^2-1}\,\vec{\mu}(\vec{r},t)$$

$$+ \frac{c^2}{\omega^2}\,\frac{\bar{N}(\beta-i\omega\gamma)}{n^2-1}\int_\Sigma \operatorname{curl}\operatorname{curl}\{\{\vec{\mu},\varphi\}\}\,d\sigma' + O\left(\frac{b}{\lambda_0}\right)^2 \quad ;$$

$$\bar{N} = \frac{N}{V} \quad . \tag{89}$$

The essence of the "Oseen process" is that the integrals over Σ, the exterior surface of the system, just cancel the terms involving the external electric intensity $\vec{E}^{(e)}$. That these latter must be canceled is apparent from the fact that they would correspond to excitation of the medium with the vacuum wave length and propagation vector, which is not observed. That the cancellation should be due to surface terms in mutually destructive fashion is physically plausible, since this leads to the effective field inside the system not depending on the form of the bounding surface, other than as determined by the refraction at the surface. Attempts to demonstrate this cancellation have been made, for example by Born[24]. If we assume this to be true and omit the explicit inclusion of the terms $O(b/\lambda_o)^2$, we find

$$\vec{\mu}(\vec{r},t) = \frac{4\pi\bar{N}\alpha}{3}\frac{n^2+2}{n^2-1}\vec{\mu}(\vec{r},t) + \frac{c}{i\omega}\frac{4\pi\bar{N}(\beta+i\omega\gamma)}{n^2-1}\nabla\times\vec{\mu}(\vec{r},t) - \frac{c}{i\omega}\frac{4\pi\bar{N}\alpha}{n^2-1}\nabla\times\vec{m}(\vec{r},t)\ , \tag{90}$$

$$\vec{m}(\vec{r},t) = \frac{4\pi\bar{N}(\beta-i\omega\gamma)}{3}\frac{n^2+2}{n^2-1}\vec{\mu}(\vec{r},t)\ . \tag{91}$$

Substituting equation (91) into (90) and writing the macroscopic polarization $\vec{P}(\vec{r},t)$, instead of the average moment per molecule, we obtain

$$\vec{P}(\vec{r},t) = \frac{4\pi\bar{N}\alpha}{3}\,\frac{n^2+2}{n^2-1}\,\vec{P}(\vec{r},t) + \frac{c}{i\omega}\,\frac{4\pi\bar{N}(\beta+i\omega\gamma)}{n^2-1}\,\nabla\times\vec{P}(\vec{r},t)$$

$$-\frac{c}{i\omega}\,\frac{4\pi\bar{N}(\beta-i\omega\gamma)}{n^2-1}\,\frac{4\pi\bar{N}\alpha}{3}\,\frac{n^2+2}{n^2-1}\,\nabla\times\vec{P}(\vec{r},t)\,. \tag{92}$$

It is evident from this equation that to terms of the order of the retardation terms β and γ

$$\frac{4\pi\bar{N}\alpha}{3}\,\frac{n^2+2}{n^2-1} = 1\,, \tag{93}$$

which is just the classical Lorenz-Lorentz formula. Thus, neglecting a term involving the squares of the retarded quantities and using equation (58), one finds

$$\vec{P}(\vec{r},t) = \frac{4\pi\bar{N}\alpha}{3}\,\frac{n^2+2}{n^2-1}\,\vec{P}(\vec{r},t) + \frac{4\pi\bar{N}}{n^2-1}\,2i\omega\gamma n\vec{s}\times\vec{P}(\vec{r},t) \tag{94}$$

If a right-handed set of orthogonal unit vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ such that $\vec{a}_3$ coincides with $\vec{s}$ is chosen and it is noted from equation (58) that $\vec{s}\cdot\vec{\mu} = 0$, equation (94) written in component form gives

$$\vec{a}_1\cdot\vec{P} = P_1 = -\frac{16\pi^2\bar{N}i\nu\gamma n}{\left(1-\frac{4\pi\bar{N}\alpha}{3}\right)\left(n^2-\frac{1+8\pi\bar{N}\alpha/3}{1-4\pi\bar{N}\alpha/3}\right)}\,P_2\,, \tag{95}$$

$$\vec{a}_2\cdot\vec{P} = P_2 = \frac{16\pi^2\bar{N}i\nu\gamma n}{\left(1-\frac{4\pi\bar{N}\alpha}{3}\right)\left(n^2\,\frac{1+8\pi\bar{N}\alpha/3}{1-4\pi\bar{N}\alpha/3}\right)}\,P_1\,. \tag{96}$$

Solution of the secular determinant gives

$$n^2 - \frac{1+8\pi\bar{N}\alpha/3}{1-4\pi\bar{N}\alpha/3} = \pm \frac{16\pi^2\bar{N}\nu\gamma n}{1-4\pi\bar{N}\alpha/3} , \tag{97}$$

and therefore

$$\frac{P_2}{P_1} = \pm i \tag{98}$$

where in equation (97) and (98) the same choice of sign, upper or lower is to be made. With the upper sign, one finds

$$Re\,\vec{P} = P_0\left[\vec{a}_1 \cos\omega\left(t - \frac{n\vec{s}\cdot\vec{r}}{c}\right) + \vec{a}_2 \sin\omega\left(t - \frac{n\vec{s}\cdot\vec{r}}{c}\right)\right], \tag{99}$$

which corresponds to left circularly polarized light: i.e., the electric vector rotates clockwise when the observer is looking in the direction of the propagation vector. Consequently equation (97) with the upper sign determines the index of refraction n_L for the left circularly polarized light.

Similarly n_R, the index of refraction for right circularly polarized light, is given by the same equation but with the lower sign.

It is convenient to define a mean refractive index by the equation

$$n_0^2 = \frac{1+8\pi\bar{N}\alpha/3}{1-4\pi\bar{N}\alpha/3} . \tag{100}$$

This is, of course, the familiar equation for the refractive index in a non-optically active, isotropic medium. From equation (97) we then obtain

$$n_L^2 - n_R^2 = \frac{16\pi^2 \bar{N} \nu \gamma (n_L + n_R)}{1 - 4\pi \bar{N} \alpha/3} \quad , \tag{101}$$

or, using equation (100),

$$n_L - n_R = 16\pi^2 \bar{N} \nu \gamma \frac{n_o^2 + 2}{3} \quad . \tag{102}$$

Equation (102) determines the circular double refraction in terms of the parameter γ of equation (44). The Fresnel formula for the rotation in radians of the plane of polarization per centimeter of travel through the medium is (λ_o in centimeters)

$$\mathcal{V} = \frac{\pi}{\lambda_o}(n_L - n_R) \quad . \tag{103}$$

In the conventional units, degrees rotation per decimeter path length,

$$\mathcal{V} = \frac{1800}{\lambda_o}(n_L - n_R) \quad , \tag{104}$$

where λ_o is still to be taken in centimeters. Using (102), the specific rotation $[\alpha]$, defined as degrees of rotation per decimeter travel per gram per cubic centimeter, is then given by

$$[\alpha] = 1800 \frac{16\pi^2 N}{\lambda_o^2 M} \frac{n_o^2 + 2}{3} g \quad , \tag{105}$$

where N is now Avogadro's number, M the gram molecular weight, and

$$g = c\gamma \tag{106}$$

Inserting numerical values we have for the specific rotation at the frequency of the sodium D line

$$[\alpha]_D = 4.930 \times 10^5 \frac{n_0^2+2}{3M} g \tag{107}$$

if g, with the dimensions of length to the fourth power, is computed with the angstrom as the unit of length.

Equation (102) is the commonly used relation between the circular double refraction and the molecular parameter γ. It will probably be well to summarize here the assumptions which have been made in the course of its establishment. From the beginning of our discussion we have assumed the effective electric field in a given molecule to be simply periodic with the frequency of the incident wave, thus ignoring the irregular fluctuations due to the motion of the surrounding molecules and their induced moments. We have neglected alterations of the distribution functions due to the presence of the light wave. The internal quantum states of a given molecule have been assumed independent of the positions and internal quantum states of the other molecules; on the other hand we have allowed the position of a given molecule to be dependent on the positions of the others. In taking account of the retardation in the fields

of the induced moments we have neglected the finite diffusion velocity of the molecules; this can hardly be expected to materially change the result, particularly because of the smallness of their velocity relative to the velocity of light, but also because of the final averaging over the positions.

The two major approximations involved in the discussion are the neglect of the fluctuation of such orientational averages as $\overline{\underline{\alpha} \cdot \vec{E}}$ from $\overline{\underline{\alpha}} \cdot \overline{\vec{E}}$, and the fluctuations of the translational averages $\overline{\text{curl curl}[\vec{\mu}]/R}$ from $\overline{\text{curl curl}}\,\overline{[\vec{\mu}]/R}$. The use of these approximations was originally set forth in explicit fashion by Kirkwood[26] in his treatment of the static electric polarization of a dielectric, in which it was shown that with these approximations the Clausius-Mossotti relation for the effective field can be derived statistical mechanically. We have not attempted to estimate the errors introduced by these approximations in the present case; Kirkwood has estimated them for the case of static polarization.

We have neglected the contributions of quadrupole and higher multipole moments to the effective electric field. In the static case it may easily be shown that in the approximation of replacing the translational average $\overline{\text{curl curl}[\vec{\mu}]/R}$ by $\overline{\text{curl curl}}\,\overline{[\vec{\mu}]/R}$, the quadrupole and higher moments make no contributions to the average effective field.

If we suppose that each of the molecular wave functions ψ_n may be sufficiently well approximated by a product of a translational wave function depending only on the coordinates and velocities of the center of mass, an electronic wave function in which the nuclear coordinates are considered fixed and appear only as parameters and a vibrational - rotational - nuclear spin wave function involving only the coordinates of the nuclei, i.e.,

$$\psi_n = \psi_{n_t}^{(t)} \psi_{n_e}^{(e)} \psi_{n_{vr}}^{(vr)} , \tag{108}$$

equation (44), defining the parameter γ, may be simplified in an illuminating fashion. First it may be readily seen that the translational quantum levels have no effect on γ: since the operators $\vec{\mu}$ and $\vec{m}$ do not contain the coordinates of the center of mass, their matrix elements contain a factor of either unity or zero, according as n and n' of equation (44) are equal or unequal; when n = n', however, $\nu^{n'n} = 0$, so that the translational quantum numbers may be omitted from both sums. The additional factoring into an electronic part and a vibrational-rotational part has the further effect of splitting γ into two terms, each of the same form as equation (44), one involving only matrix elements of the nuclear part of the dipole moment and magnetic moment operators with the nuclear wave functions, the other involving only matrix elements of the electronic part of the dipole

moment with the electronic wave functions.

The nuclear part of γ will in general be small, because of the large masses of the nuclei compared to those of the electrons. In agreement with this expectation, measurements in the infra-red have obtained no indication of rotatory dispersion due to the infra-red absorption bands[28,29]. Furthermore usually only the ground electronic state will have an appreciable Boltzmann factor at room temperatures, so that the averages over electronic energy states will be superfluous. With these approximations we may write the equation in the simple form

$$\gamma = \frac{1}{3\pi h} \sum_n \frac{\mathrm{Im}[\vec{\mu}_{on} \cdot \vec{m}_{no}]}{\nu_{no}^2 - \nu^2} \quad , \tag{109}$$

where the electronic ground state is indicated by the index zero. The sum is over all excited electronic states, the electronic wave functions being for fixed nuclei in the field-free state. The matrix elements are now numbers, rather than matrices, so the über-matrix notation has been abandoned.

Kirkwood[18] has shown how an important decomposition of equation (109) may be achieved. It is convenient to consider the molecule as composed of N substituent groups coupled to a central N + 1th group. It is supposed that each electron in the molecule may be unambiguously assigned to one or the other of the N + 1 groups. Evidently if resonance between substituent groups is absent, there will be no ambiguity in the assignment of non-bonding electrons

between substituent groups. The partition of bonding electrons between the central group and the various substituent groups is less direct, but we may suppose as an adequate approximation that the bonding electrons are in each case divided equally between the central group and the corresponding substituent group.

Indicating the position of electron s of group k with respect to the center of mass of group k by $\vec{r}_s$ and the position of the center of mass of group k relative to the center of mass of the molecule by $\vec{R}_k$, we have for the electronic part of the electric moment of the molecule as a whole

$$\vec{\mu} = \sum_{K=1}^{N+1} \vec{\mu}^{(K)} + e \sum_{K=1}^{N+1} \sum_{s}^{(K)} \vec{R}_K \ ,$$

$$\vec{\mu}^{(K)} = \sum_{s}^{(K)} e \vec{r}_s^{(K)} \ . \tag{110}$$

In equation (110) the notation $\sum_s^{(K)}$ means a summation over all the electrons of group k. Similarly, the magnetic moment of the molecule as a whole may be written as

$$\vec{m} = \sum_{K=1}^{N+1} \vec{m}^{(K)} + \frac{e}{2mc} \sum_{K=1}^{N+1} \vec{R}_K \times \vec{p}^{(K)} \ ,$$

$$\vec{m}^{(K)} = \frac{e}{2mc} \sum_{s}^{(K)} \vec{r}_s^{(K)} \times \vec{p}_s$$

$$\vec{p}^{(K)} = \sum_{s}^{(K)} \vec{p}_s \tag{111}$$

where $\vec{p}_s$ is the momentum of electron s.

It is immediately seen that the term containing $\vec{R}_k$ in equation (110) drops out on substitution in equation (109) because of the orthogonality property of the wave functions. Substituting equations (110) and (111) into (109), we obtain

$$g = g^{(0)} + g^{(1)} + \sum_{K=1}^{N+1} g_K \quad ,$$

$$g^{(0)} = -\frac{c}{6\pi i \hbar}\frac{e}{2mc}\sum_{n}{}'\sum_{\substack{i,K=1 \\ i\neq K}}^{N+1}\frac{\vec{R}_K\cdot\left[\vec{\mu}_{on}^{(i)}\times\vec{p}_{no}^{(K)} - \vec{\mu}_{no}^{(i)}\times\vec{p}_{on}^{(K)}\right]}{\nu_{no}^2-\nu^2} \quad ,$$

$$g^{(1)} = \frac{c}{3\pi\hbar}\sum_{n}{}'\sum_{\substack{i,K=1 \\ i\neq K}}^{N+1}\frac{\mathrm{Im}\left\{\vec{\mu}_{on}^{(i)}\cdot\vec{m}_{no}^{(K)}\right\}}{\nu_{no}^2-\nu^2} \quad ,$$

$$g^{(K)} = \frac{c}{3\pi\hbar}\sum_{n}{}'\frac{\mathrm{Im}\left\{\vec{\mu}_{on}^{(K)}\cdot\vec{m}_{no}^{(K)}\right\}}{\nu_{no}^2-\nu^2} \quad . \qquad (112)$$

Here the prime on the summations over electronic states means that the ground state n = 0 is to be omitted; the term corresponding to the latter is evidently zero in any case. Analogous to equation (25), we have the relation

$$e\vec{p}^{(K)} = 2\pi i \nu_{no} m \vec{\mu}_{no}^{(K)} \quad , \qquad (113)$$

which permits $g^{(0)}$ to be written in the form

$$g^{(0)} = -\frac{1}{6h}\sum_{n}{}'\sum_{\substack{i,K=1 \\ i\neq K}}^{N+1}\frac{\nu_{no}}{\nu_{no}^2-\nu^2}\,\vec{R}_K\cdot\left[\vec{\mu}_{on}^{(i)}\times\vec{\mu}_{no}^{(K)}+\vec{\mu}_{no}^{(i)}\times\vec{\mu}_{on}^{(K)}\right] \tag{114}$$

It may be mentioned that while the operators in equations (112) and (114) are those associated with the electrons of a given group, the wave functions with which the matrix elements are computed are those for the entire molecule.

The sign of $g^{(0)}$ as given by equation (114) is opposite to that originally obtained by Kirkwood, due to an error in sign in the third of equations (16) in his paper.

Subject to the accuracy with which it is possible to consider each of the electrons of the molecule as associated with a particular group, equations (112) and (114) are equivalent to equation (109). The term $g^{(0)}$ evidently corresponds to the interaction of the dipole moments of different groups, while $g^{(1)}$ is characterized by coupling of the magnetic moment of one group with the electric moments of another. The terms g_K, one for each of the groups, correspond to the interaction of the electric and magnetic moments induced in the same group.

SECTION III

POLARIZABILITY THEORIES OF OPTICAL ACTIVITY; APPLICATION TO THE DETERMINATION OF THE ABSOLUTE CONFIGURATIONS OF OPTICALLY ACTIVE MOLECULES

Part I: The polarizability theories of Gray, de Mallemann and Boys

It is convenient to designate as polarizability theories those which relate the optical rotatory power of a molecule to the optical polarizabilities of the atoms or groups of atoms composing the molecule. The first of these theories was developed by Gray[13], who showed that a molecular model consisting of polarizable atoms, each considered concentrated at a point, would exhibit optical activity providing the molecule was dissymmetric. Gray discussed only the specific case of a molecule consisting of five atoms, four atoms being at the corners of an irregular tetrahedron, the fifth inside the tetrahedron, corresponding to such a compound as CHIBrCl. He considered the atoms to be isotropic <u>per se</u>, the induced moment in each atom being in the direction of the total electric field acting on that atom. The equations are exceedingly complex, and he did not succeed in obtaining a formula compact enough to be completely written down. Perhaps because of this, he did not perform explicit calculations for a definite molecule. Gray's treatment is of interest only in that it was the first of the polarizability theories.

The polarizability theories may properly be called specializations of the Born coupled oscillator theory[11]. The latter was very general in that no explicit assumptions

were made about the molecular structure other than that oscillators were present, spatially separated, and some sort of coupling existed between them. Nothing was said about the location of the oscillators or the nature of the coupling. The theory was therefore a very general one, but precisely because of the generality it was not suitable for calculation of the optical activity of a given molecule without specialization of some sort. The polarizability theories correlate the polarizability of the various groups with oscillators assumed localized within the group, the coupling being assumed to be produced through the electromagnetic fields of the induced moments of the oscillators.

Theories similar to Gray's have been developed by de Mallemann[15] and by Boys[16]. The term considered by Boys is essentially the same as the one treated by Gray, the molecule being considered as consisting of a number of isotropic polarizable atoms (or groups of atoms) whose moments may be represented by point dipoles. The complicated problem of the interaction of the induced moments in the different groups is attacked by means of a method of successive approximations. The moment induced in each group is treated as a sum of terms corresponding to the order of interaction with the moments of the other groups. Considering a given group D, the zero-order term is the moment induced in D by the external field alone, with

neglect of the scattered radiation from the other groups. This may be called, in Boys' nomenclature, a "relay system of zero order", indicated by {D}. The first-order term corresponds to the moment induced in D due to the part of the moment of each of the other molecules which is induced by the external field alone. Such a term is denoted by {CD}; for given D there would be a term of this order for each choice of the other groups as C. Similarly, the third-order contribution to the moment of group D, indicated by {BCD}, is induced by that part of the moment in group C which is itself due to the portion of the moment of a third group B induced by the external field alone. As might be anticipated the magnitude of the contributions to the total moment decreases rapidly in the higher order relays. It is found that with isotropic groups the relays {D}, {CD}, and {BCD} do not result in optical activity, the first relay producing this phenomenon being {ABCD} involving four groups. Higher order terms such as {ZABCD} will also contribute to the optical rotation but may be expected to be small compared to the fourth-order terms.

Boys developed a compact formula for a molecule composed of four groups A, B, C and D, but its applicability is somewhat limited by assumptions he made concerning molecular structure. The groups were taken to be spheres, with radii corresponding approximately to the presently accepted "normal covalent radii". However he supposed the four groups to arrange themselves in a fashion determined

only by closest packing of the four spheres. In applying his theory Boys treated an optically active compound such as sec-butyl alcohol as being composed of five groups, namely, the asymmetric carbon atom and its four substituent groups. The size and polarizability of the asymmetric carbon atom were apportioned equally among the four substituents, and a four-atom model applied.

The assumption of close packing of the four spheres permits the six inter-group distances to be specified in terms of the radii of the four spheres. In actual molecules the six distances can vary independently and so cannot be specified by four distances. Often however four distances can be chosen, the sums of pairs of which reproduce the six actual inter-group distances fairly well, and use made of Boys' formula in this fashion. The assumption of close packing coupled with the values taken for the radii by Boys lead, as pointed out by Kirkwood[18], to a wholly untenable structure, the worst feature being that in sec-butyl alcohol, for example, the resulting linear dimensions of the molecule are approximately only two-thirds those indicated by modern structural knowledge. Because in Boys' formula the specific rotation is inversely proportional to the eighth power of this linear scale factor, Boys considerably overestimated the magnitude of his term. Thus for sec-butyl alcohol he obtained a value roughly 140 times larger than that indicated by present structural knowledge. It seems

likely that in most cases the Boys term will be too small to account for an appreciable part of the observed optical activity.

The classical polarizability theory has also been discussed at some length by de Mallemann[15]. He considered the various terms contributed to the optical activity by interactions of two anisotropic groups, of three groups one of which is anisotropic, and of four isotropic groups. The latter is the same term as calculated by Boys; de Mallemann did not make the same simplifying assumptions as did Boys, however, so that his relation is somewhat more complex. The first-mentioned term is essentially the same as that calculated by Kirkwood and described in the next section. De Mallemann did not apply his theory to the actual calculation of optical activity for specific molecules.

Part II: The polarizability theory as developed by Kirkwood

The theories of Gray, Boys and de Mallemann, as is evident from the preceding discussion, were based on classical mechanics. Kirkwood[18] has shown how the polarizability theories may be obtained from the $g^{(0)}$ term of the quantum mechanical equations (112) and (114). The hypotheses of Gray and Boys regarding the isotropy of polarizability of the groups composing the molecules are probably incorrect, as it seems likely that the formation of a chemical bond will provide perturbation of an originally spherical atom sufficient to establish at least one preferential direction of polarization. Since lower order "relay systems" suffice to give optical activity when anisotropic groups are involved, and since these lower order terms do not fall off as rapidly with increasing distances between the groups as do the higher order terms required with isotropic groups, it seems clear that in general the most important term of the polarizability theory was not considered by these authors. De Mallemann obtained formulas for anisotropic groups but did not use them in actual calculations. The latter was first attempted by Kirkwood[18], who obtained these anisotropic terms from a quantum mechanical treatment of the $g^{(0)}$ term of equation (112). Because attempts at assigning absolute configurations to several organic compounds on the basis of this first-order term of the polarizability theory are to be

described, it will be of interest to sketch the method used by Kirkwood in obtaining his final formulas.

The problem is the computation of $g^{(0)}$ as given by equation (112), which evidently requires knowledge of the molecular electronic wave functions. Approximations to these are obtained formally by means of the usual first-order perturbation theory, it being supposed that the following zero-order problem has been solved. The molecule is considered as being composed of N + 1 groups, N of which are bonded to the N + 1^{th} group, which is called the central group. The zero-order wave functions just mentioned are to be solutions of an approximate Hamiltonian in which electron exchange is in every case excluded between each pair of the N + 1 groups, and in which all interactions among the N substituent groups are excluded. Exchange within the various groups, and the coulomb interaction between the central group and each of the N substituent groups are supposed included in this zero-order Hamiltonian, in a generalized "self-consistent field" approximation. This permits the zero-order wave function for each electronic level to be written as a product of N + 1 group wave functions, each of which contains as variables only the coordinates of the electrons of one of the groups:

$$\mathring{\psi}_n = \prod_{i=1}^{N+1} \varphi_{n_i}\left(\vec{r}_1^{(i)}, \vec{r}_2^{(i)} \ldots .\right) \tag{115}$$

Each quantum state of the molecule as a whole may then be

specified by a set of N + 1 group quantum numbers n_i, i = 1...N + 1, which we shall indicate simply by the letter n. The zero-order frequencies will then be given by

$$\nu_{no} = \sum_{i=1}^{N+1} \nu_{n_i o} \tag{116}$$

We will use the subscript zero to represent the set of the group quantum numbers specifying the electronic ground state of the whole molecule as well as any one of these ground state group quantum numbers.

The potential energy of dipole-dipole interaction between the N substituent groups is then introduced as the first-order perturbation in the Hamiltonian,

$$V = \sum_{\substack{i,j=1 \\ i>j}}^{N} V_{ij} \quad ,$$

$$V_{ij} = \vec{\mu}^{(i)} \cdot \underline{\underline{T}}_{ij} \cdot \vec{\mu}^{(j)} \quad ,$$

$$\underline{\underline{T}}_{ij} = \frac{1}{R_{ij}^3} \left[\underline{\underline{1}} - 3 \frac{\vec{R}_{ij} \vec{R}_{ij}}{R_{ij}^2} \right] \quad ,$$

$$\vec{R}_{ij} = \vec{R}_j - \vec{R}_i \tag{117}$$

Thus electron exchange among the N + 1 groups is completely ignored in both the zero-order and the first-order stages. Consequently our wave functions may be expected to be poor representations of the valence bonds between the central and substituent groups, and therefore poor approximations for use in calculating any property of the molecule, such as bond energies, to which the bonding electrons make predominate contributions. Similarly the energy differences between levels in which the quantum states of these bonding electrons change appreciably may be poorly approximated. On the other hand, for properties to which all the electrons contribute approximately equally, such as the refractive index, the present analysis should give a reasonable estimate, as the number of electrons bonding substituent groups to the central group will generally be small compared to the total number of electrons. Similarly, unless these bonding electrons contribute excessively to the $g^{(o)}$ term, which seems unlikely, our approximations should give a reasonable estimate of the optical activity.

If the $\mathring{\psi}_n$ are degenerate we suppose the set diagonalizing V of equation (117) to have been chosen. By means of equation (115), molecular matrix elements of a function of the coordinates of a single group, such as $\vec{\mu}^{(i)}_{n'n}$, may be written as group matrix elements:

$$\vec{\mu}^{(i)}_{n'n} = \vec{\mu}^{(i)}_{n_i' n_i} \prod_{\substack{j=1 \\ \neq i}}^{N+1} \delta_{n_j' n_j} \, . \tag{118}$$

With use of equations (115 - 118) and the usual first-order perturbation theory, we find for the perturbed wave functions

$$\Psi_n = \mathring{\Psi}_n - \frac{1}{\hbar} \sum_{\ell > j=1}^{N} \sum_{n'_\ell, n'_j}{}' \frac{(V_{j\ell})_{n'_j n'_\ell ; n_j n_\ell}}{\nu_{n'_j n_j} + \nu_{n'_\ell n_\ell}} \left(\prod_{\substack{r=1 \\ \neq j,\ell}}^{N+1} \varphi_{n_r} \right) \varphi_{n'_\ell} \varphi_{n'_j} \, . \tag{119}$$

The final formulas are much simpler when real, rather than complex, zero-order wave functions are taken in equation (115). That this is in fact possible follows from the fact that the Hamiltonian operator does not contain $i = \sqrt{-1}$ except in squares in case no external magnetic field is present. It is then readily seen that if a complex function is a solution of the Schrodinger equation with a given energy eigenvalue, then both the real and imaginary parts must also be eigenfunctions corresponding to the same eigenvalue. If a level is nondegenerate, this argument shows the wave function for that level is necessarily real, barring a possible complex multiplying constant of modulus one. If a level is degenerate, then a real set of orthonormal wave functions can obviously be chosen. Furthermore, since the potential energy of equation (117) is real, it can be diagonalized with a set of real wave functions for each degenerate level, these sets then being the "correct zero-order wave functions" for use in equation (119).

It is readily seen that because of the characteristics of our zero-order wave functions as given by (118), the zero-order term of (114) calculated with these wave functions vanishes. Calculation of $g^{(0)}$ correct to first-order terms, with use of the fact that the group wave functions (and therefore the matrix elements of the group dipole moment operators) are real, gives

$$g^{(0)} = \frac{2}{3\hbar^2} \sum_{\substack{i,\kappa=1 \\ i\neq\kappa}}^{N} {\sum_{n_i}}' {\sum_{n_\kappa}}' \frac{\nu_{n_i 0}\, \nu_{n_\kappa 0} \left(\vec{\mu}^{(i)}_{n_i 0} \cdot \underset{\sim}{T}_{i\kappa} \cdot \vec{\mu}^{(\kappa)}_{n_\kappa 0} \right) \left(\vec{R}_\kappa \cdot \vec{\mu}^{(i)}_{n_i 0} \times \vec{\mu}^{(\kappa)}_{n_\kappa 0} \right)}{\left(\nu_{n_i 0}^2 - \nu^2 \right) \left(\nu_{n_\kappa 0}^2 - \nu^2 \right)} .$$

(120)

It is instructive to notice that the polarizability tensor of the molecule, in the zero-order approximation, is given by

$$\underset{\sim}{\alpha} = \sum_{i=1}^{N+1} \underset{\sim}{\alpha}^{(i)} ,$$

$$\underset{\sim}{\alpha}^{(i)} = \frac{2}{\hbar} {\sum_{n_i}}' \frac{\nu_{n_i 0}\, \vec{\mu}^{(i)}_{0 n_i}\, \vec{\mu}^{(i)}_{0 n_i}}{\nu_{n_i 0}^2 - \nu^2} .$$

(121)

That this may be expected to be a rather good approximation is suggested by the well-known additivity of atomic refractivities. It may be mentioned that the nature of these

zero-order wave functions for the groups assumes that at least a part of the empirical variation in atomic refractivity with the nature of the particular atom's chemical bonds (e.g., the difference in the Eisenlohr refractivities for oxygen depending on whether the atom is in a hydroxyl group or a carbonyl group) has in principle been taken into account.

Using equation (121), $g^{(o)}$ may be written in the form

$$g^{(o)} = \sum_{\substack{i,K=1 \\ i \neq K}}^{N} \overline{(\vec{a}_1 \cdot \vec{R}_K)(\vec{a}_2 \cdot \underline{\alpha}^{(i)} \cdot \underline{T}_{iK} \cdot \alpha^{(K)} \cdot \vec{a}_3)} \quad , \tag{122}$$

where the average is over all orientations of the nuclear framework relative to a set of external orthonormal vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$. If the group polarizability tensors are written in their principal axis representations

$$\underline{\alpha}^{(i)} = \sum_{r=1}^{3} \alpha_{rr}^{(i)} \vec{b}_r^{(i)} \vec{b}_r^{(i)} \quad , i = 1, \cdots\cdots N \, , \tag{123}$$

where the $\vec{b}_r$, r = 1,2,3, are orthogonal unit vectors, $g^{(o)}$ may be expressed in the form

$$g^{(o)} = \frac{1}{6} \sum_{\substack{i,K=1 \\ i \neq K}}^{N} \sum_{r,s=1}^{3} \alpha_{rr}^{(i)} \alpha_{ss}^{(K)} \left(\vec{b}_r^{(i)} \cdot \underset{\sim}{T}_{iK} \cdot \vec{b}_s^{(K)} \right) \vec{R}_K \cdot \vec{b}_r^{(i)} \times \vec{b}_s^{(K)} \, .$$

(124)

This is the first-order expression for $g^{(o)}$ in terms of the polarizability tensors of the substituent groups and the geometry of the molecule. The sign in equation (124), as well as in several of the preceding expressions for $g^{(o)}$, are the reverse of those in Kirkwood's original paper, due to his error in sign mentioned in Section I. Kirkwood[18] has indicated how the second-order term corresponding to de Mallemann's treatment of the interaction of three groups may be obtained, as well as the third-order term corresponding to Boys' treatment.

Equation (124) is the expression for the first-order term of the polarizability theory, applicable to any molecule to which the plausible assumptions already introduced may be applied. Unfortunately present knowledge of the group polarizability tensors is not usually sufficient to make application of the formulas possible. Structural difficulties may also present themselves, particularly in molecules having one or more internal rotations. The points will be discussed at greater length below. In the special case

when all the N groups have an axis of optical symmetry the formula may be further simplified to

$$g^{(0)} = \frac{1}{6} \sum_{\substack{i,K=1 \\ i>K}}^{N} \alpha_i \alpha_K \beta_i \beta_K \left(\vec{b}_i \cdot \underline{T}_{iK} \cdot \vec{b}_K \right) \left(\vec{R}_{iK} \cdot \vec{b}_i \times \vec{b}_K \right) ,$$

(125)

where $\vec{b}_i$ is a unit vector in the direction of the axis of optical symmetry of group i; α_i is the mean polarizability of group i, equal to one-third the trace of $\underline{\alpha}^{(i)}$. The anisotropy ratio of group i, denoted by β_i, is given by

$$\beta_i = \frac{\alpha_{\parallel}^{(i)} - \alpha_{\perp}^{(i)}}{\alpha_i} ,$$

(126)

in which $\alpha_{\parallel}$ indicates the polarizability of group i parallel to its cylindrical axis, $\alpha_{\perp}^{(i)}$ the polarizability perpendicular to this axis.

From equation (109) we see that $g^{(0)}$ can be written in the form

$$g = \frac{c}{3\pi h} \sum_{n} \frac{R_{on}}{\nu_{no}^2 - \nu^2} ,$$

$$R_{on} = Im \left[\vec{\mu}_{on} \cdot \vec{m}_{no} \right] .$$

(127)

One sees immediately that the R_{on}, called the rotatory strengths, satisfy the important sum rule

$$\sum_n g_{on} = Im\left\{\sum_n \vec{\mu}_{on}\cdot\vec{m}_{no}\right\} = Im\left\{(\vec{\mu}\cdot\vec{m})_{oo}\right\} = 0 \quad , \tag{128}$$

inasmuch as the diagonal elements of $\vec{\mu}\cdot\vec{m}$ must be real, this operator being Hermitian because $\vec{\mu}$ and $\vec{m}$ commute and are Hermitian themselves. Inasmuch as the sum is zero, positive and negative terms must both occur among the R_{on}. A consequence of this is that often the rotatory power in the visible region of the spectrum is controlled by a very few of the near-ultraviolet absorption bands. The contributions of bands farther in the ultraviolet, although possibly having appreciable R_{on}, become small due to the higher frequencies in the denominator and may tend to cancel because of different signs. The latter is important because otherwise the behavior would be similar to that observed for the polarizability, where the far-ultraviolet terms may be small, but obey a different sum rule. The somewhat similar expressions for the mean polarizability are

$$\alpha = \frac{2}{3\hbar} \sum_n \frac{\nu_{no}\, \vec{\mu}_{on} \cdot \vec{\mu}_{no}}{\nu_{no}^2 - \nu^2} = \frac{e^2}{4\pi^2 m} \sum_n \frac{f_{on}}{\nu_{no}^2 - \nu^2} \ ,$$

$$f_{on} = \frac{8\pi^2 m}{3e^2\hbar}\, \nu_{no}\, \vec{\mu}_{on} \cdot \vec{\mu}_{no} \ ,$$

(129)

where the f_{on} are called the oscillator strengths, and N_e is the total number of electrons in the molecule. The expression for $g^{(o)}$ given in equation (114) may be written in similar form

$$g^{(o)} = \frac{1}{6\hbar} \sum_n \frac{g_{on}^{(o)}}{\nu_{no}^2 - \nu^2} \ ,$$

$$g_{on}^{(o)} = -\sum_{\substack{i,K \\ i \neq K}}^{N} \nu_{no}\, \vec{R}_K \cdot \left(\vec{\mu}_{on}^{(i)} \times \vec{\mu}_{no}^{(K)} + \vec{\mu}_{no}^{(i)} \times \vec{\mu}_{on}^{(K)} \right) ,$$

$$\sum_n g_{on}^{(o)} = 0 \ .$$

(130)

The treatment so far has been based on the tacit supposition that only one relative configuration of the nuclei requires consideration. In cases where several stable nuclear configurations are possible, as for instance in molecules having several potential minima associated with one or more internal rotations, a statistical average is to be taken over the torsional vibrational states.

Probably the most interesting application of equation (125) lies in its possible use in establishing absolute configurations for organic compounds. However, it is necessary to keep in mind that $g^{(o)}$ is only a part of the total rotatory parameter g, as given by equation (112). It is worth-while to point out that if the difference in phase of the electromagnetic field at the different groups is considered, but the phase everywhere within each group is approximated by the phase at the center of mass of that group, then $g^{(1)}$ and all the g_k vanish, leaving only $g^{(o)}$. Thus $g^{(o)}$ may be expected to be an increasingly good approximation to g as the sizes of the groups become small compared to the intergroup distances. Nevertheless it is not possible to say that the negligibility of $g^{(1)}$ and the g_k in actual molecules has been demonstrated, particularly so since Eyring and his co-workers[22,29,30] have made attempts to calculate some of the latter in special cases of certain molecules. Attempts were made in the present series of researches to find alternative ways of estimating these other terms, but without success. At present there seems no other way than actually attempting to find molecular wave functions (excited as well as ground state) accurate enough to give good approximations to the matrix elements entering the formulas. This is the method of Eyring and his co-workers, which will be discussed in Section IV.

In applying Kirkwood's polarizability theory just outlined, it is necessary to know the polarizability tensors of the groups, i.e., the principal polarizabilities and the principal axes of each group, as well as the geometrical structure of the molecule. As mentioned before, present knowledge regarding the first point in practice restricts one to molecules in which the substituent groups are cylindrically symmetrical. Even here, as will be presently shown, difficulties are found.

It will be recalled that the zero-order polarizability tensors, to which α_i and β_i of equation (125) refer, include interaction of substituent group i with the central group, and include the effects of interaction of group i with the other substituent groups only through interaction of the latter with the central group themselves. These effects might be expected to be small, so that to a good approximation the zero-order polarizability tensor of a given substituent group bonded to a given central group may be expected to be the same from molecule to molecule, as is indicated by the success of the rule of additivity of atomic refractivity.

The mean polarizability α_i of equation (125) may be obtained from the well known Eisenlohr[31] atomic refractivities,

$$\alpha_i = \frac{3}{4\pi N} \sum_r^{(i)} A_r \quad , \tag{131}$$

where N is Avogadro's number, A_r is the Eisenlohr atomic refractivity of atom r of group i, and the sum goes over the atoms of group i.

The determination of the anisotropy ratios of the various groups is more difficult. For this purpose the results of two different optical experiments are useful, namely, measurements of the degree of depolarization of scattered light and measurements of the Kerr constant. The degree of depolarization Δ of Rayleigh light scattering perpendicular to the direction of the incident beam, the latter being unpolarized, is related[32] to the principal polarizabilities by the formula

$$\beta^2 = \frac{(\alpha_{11}-\alpha_{22})^2+(\alpha_{22}-\alpha_{33})^2+(\alpha_{33}-\alpha_{11})^2}{2\alpha^2} = \frac{45\Delta}{6-7\Delta}$$

$$\alpha = \frac{1}{3}(\alpha_{11}+\alpha_{22}+\alpha_{33}).$$

(132)

The quantity β is called the optical anisotropy of the molecule. For a cylindrically symmetrical molecule the equations become

$$\beta^2 = \frac{(\alpha_{11}-\alpha_{\perp})^2}{\alpha^2} = \frac{45\Delta}{6-7\Delta} \quad ,$$

$$\alpha = \frac{1}{3}(\alpha_{11}+2\alpha_{\perp}) \quad ,$$

(133)

which is equivalent to equation (126), but it is evident that knowledge of Δ and α determines the magnitude but not the sign of β. The mean polarizability α may be computed either from the Eisenlohr atomic refractivities or the measured index of refraction by means of the relation

$$\alpha = \frac{n-1}{2\pi \bar{N}} \quad , \tag{134}$$

n being the refractive index, $\bar{N}$ the number density of the molecules.

In many cases however the sign of β can be predicted with confidence from the geometry of the molecule by use of arguments due originally to Silberstein[33]. Thus in the case of a diatomic molecule supposed to consist of two isotropic polarizable point masses, an external field applied along the figure axis results in induced moments which reinforce each other, while an external field perpendicular to the axis induces moments whose fields oppose each other. On this basis the figure axis should be the axis along which the polarizability of the molecule is greatest, or in other words the polarizability ellipsoid of a diatomic molecule should always be prolate. Since the dipole moment of a diatomic molecule must lie along the figure axis, the usual theory of the Kerr effect[34,35] leads to the conclusion that diatomic molecules would not be expected to have a negative Kerr constant, in agreement with experiment. Considerations of this kind may be applied in qualitative fashion to polyatomic molecules. The cases of methyl chloride

and chloroform are examples. Both have a threefold axis of symmetry, along which the dipole moment must lie. In methyl chloride the polarizability along the axis would be expected to be greater than that perpendicular to it, as it appears that of the various interactions only those involving hydrogen with hydrogen would favor the opposite possibility. In the case of chloroform however the greater polarizability of the chlorines may be expected to result in the polarizability perpendicular to the symmetry axis being the greatest. The correctness of this conclusion is verified by the observation that chloroform has a negative Kerr constant, methyl chloride a positive one. In general, it may be supposed that these Silberstein arguments will give correct qualitative results; rigorously accurate statements require quantum mechanical calculation of the polarizabilities, which is not practicable.

Quantitative information may also be obtained from the Kerr effect, or electrical double refraction. If $n_{\parallel}$ and $n_{\perp}$ represent the refractive indices of light polarized parallel and perpendicular, respectively, to the applied electrostatic field E_o in the Kerr experiment, for not too large values of the latter a quadratic dependence of the electrical double refraction on the field strength holds according to relation

$$\frac{n_{\parallel} - n_{\perp}}{n} = K E_o^2 \qquad (135)$$

n being the index of refraction for the field-free medium, while K, the constant of proportionality, is called the Kerr constant[35].

For gases and vapors at not too high pressures, so that n≈1, it may be shown[35] that the Kerr constant is related to the principal polarizabilities and dipole moment by the equations

$$K = K_1 + K_2$$

$$K_1 = \frac{(\epsilon-1)(n-1)\beta^2}{60\pi\bar{N}kT}$$

$$K_2 = \frac{\pi\bar{N}\mu^2(2\alpha_3-\alpha_2-\alpha_1)}{15k^2T^2} \qquad (136)$$

for the special case where the direction of the dipole moment coincides with one of the principal optical axes, which we denote by the subscript 3. Here ϵ is the static dielectric constant, n the refractive index for the field-free medium at the frequency of light used in the experiment, β the anisotropy as given by equation (132), $\bar{N}$ the average number of molecules per unit volume, μ the magnitude of the permanent dipole moment.

In molecules not having a permanent dipole moment K_2 is zero, and from knowledge of K_1, ϵ, and n, the anisotropy ratio β may be calculated (apart from its sign), a check

thus being obtained on the values found in the measurements of depolarization of scattered light. In molecules having permanent dipoles, unless the latter are very small, K_2 is usually much greater than K_1. The latter may be estimated from the experimental depolarization of scattered light, and K_2 then obtained from K using this result. The separation of K_1 and K_2 may also be achieved by measuring the temperature dependence of K. If the latter is plotted against the reciprocal of the absolute temperature a straight line should result; K_1 (i.e., β) may be estimated from the intercept and K_2 (i.e., $2\alpha_3-\alpha_2-\alpha_1$) from the slope.

If the molecule, besides having its dipole (if any) along one of the principal axes of polarizability, is also cylindrically symmetrical (the axis of symmetry necessarily being that along which the dipole moment lies), the anisotropy ratio β can be determined from measurements of the refractive index and of the Kerr constant at a single temperature, without reference to the depolarization measurements, because K_1 and K_2 then depend on the same function of the principal polarizabilities.

Recapitulating, the measurements of the Kerr constant or the depolarization of scattered light, or both, for suitable molecules, leads to information regarding the polarizability tensors of the molecules. In molecules having no dipole moment, the measurement of the Kerr constant and degree of depolarization both provide estimates of the

anisotropy ratio β . The latter and the mean polarizability α determined from measurement of the refractive index give two relations between the three principal polarizabilities. If two of the latter are equal (cylindrical symmetry), the values of the principal polarizabilities are determined, but not their assignment to directions parallel and perpendicular to the symmetry axis. The latter may usually be deduced from the Silberstein arguments. If the molecule has a dipole moment lying along one of the principal polarizability axes, as is often required by symmetry, then measurements of the refractive index, degree of depolarization, and Kerr constant determine the polarizability in the direction of the dipole moment uniquely, as well as the values of the polarizabilities along the other two axes, but not the assignment of the latter two values to the one or the other of their axes. Here again, the Silberstein criteria may make possible the removal of this ambiguity.

Thus in the case of cylindrically symmetrical molecules, possibly with qualitative use of the Silberstein theory, we can determine the polarizability ellipsoid. Proceeding from this to the polarizability ellipsoid of the groups which we may regard as composing the molecule requires further assumptions. It has been mentioned that the zero-order wave functions used by Kirkwood result in additivity of the polarizability tensors of the groups giving the polarizability tensors of the molecule in the zero-order. The

theory as formulated by Kirkwood specifies these group polarizability tensors as including the effects of coulombic interaction between the given group and the central group, and we have mentioned how this still results in a dependence of the polarizability tensor of a given group on the nature of the other substituents in the central group, stating however that this dependence might be slight, and its neglect not serious. In practice, this and still further assumptions are necessary.

In estimating the group anisotropies we have followed the procedure used by Kirkwood[18]. Considering the molecule of ethane as composed of two methyl groups, each of which have the direction of the carbon-carbon bond as an axis of cylindrical symmetry, on the basis of the above assumption it is readily seen that $\beta_{CH_3} = \beta_{C_2H_6}$, β_{CH_3} being the anisotropy of the methyl group, $\beta_{C_2H_6}$ the anisotropy computed for ethane from the degree of depolarization of scattered light or from the Kerr constant. On the basis of the qualitative Silberstein theory, $\beta_{C_2H_6}$ should be positive, and therefore β_{CH_3} also. This is the anisotropy of a methyl group bonded to a methyl group, and therefore not of immediate applicability to methyl groups in compounds other than ethane. However, if the further approximation of considering the anisotropy of the methyl group to have the same values in other compounds, such as methyl chloride, is made, then use of the observed values of

the anisotropy ratios of such other compounds permits the determination of the anisotropy of other groups, such as chlorine. This assumption, though not without its difficulties, seems to be the only feasible one if actual quantum mechanical calculations are to be avoided. For groups such as the phenyl radical which may be expected to have a large intrinsic anisotropy, apart from the effects of interaction with the central group (in contrast to chlorine, for instance), it appears reasonable to proceed again in a way utilized by Kirkwood, namely, to treat the group in question as having the symmetry and numerical anisotropy of the parent hydrogen compound - in the case of the phenyl group, benzene.

A practical difficulty is encountered in that measurements of the degree of depolarization of light scattered by molecules in gases and vapors are experimentally quite difficult owing to the smallness of the effect, and different values are often obtained by different investigators. The experimental degrees of depolarization and Kerr constants for several compounds are shown in Table I, with the calculated values of the anisotropy ratios.

The uncertainty in the anisotropy of ethane is particularly troublesome, inasmuch as the resulting uncertainty in the anisotropy of the methyl group results in uncertainties in the anisotropies of other groups obtained using the former value. The values obtained using the different sets of measurements are shown in Table 2. It is seen that

Compound	Light Scattering			Kerr Effect		
	Δ	Observer	β, calc. from Δ	K x 10^{15}	Observer	β, calc. from K
Ethane, C_2H_6	0.016	Cabannes (36)	0.35	0.5	Stuart (35)	0.29*
	.005	Anantha-krishnan (37)	.19	.67	Breazeale (38)	.33*
Methyl chloride, CH_3Cl	.015	Cabannes (36)	.35	36.5	Stuart (35)	.33**
	.020	Anantha-krishnan (37)	.39			
Methyl bromide, CH_3Br			.41	45.5	Stuart (35)	.37***

* Calculated using $n_{5460}^{S.T.P.}$ 1.000769; $\epsilon^{S.T.P.} = 1.00150$

** Calculated using $\mu =$ 1.86 x 10^{-18} e.s.u.; $n_{5460}^{S.T.P.}$ 1.000780

*** Calculated using $\mu =$ 1.80 x 10^{-18} e.s.u.; $n_{D}^{S.T.P.}$ 1.000964

TABLE I

TABLE II

Source of experimental values	Group	Group anisotropy ratio
Ananthakrishnan, light scattering	CH_3	0.19
	Cl	.59
	Br	.55*
	CH_2Cl	.39**
Cabannes, light scattering	CH_3	0.35
	Cl	.35
	CH_2Cl	.35**
Stuart, Kerr constant	CH_3	0.31***
	Cl	.35
	Br	.41
	CH_2Cl	.33**,***
	CH_2Br	.37

* Ananthakrishnan did not determine Δ for CH_3Br; calculated with his value for CH_3 and an estimated Δ for CH_3Br of 0.022

** Taken as equal to the anisotropy ratio of CH_3X

*** Average of Stuart's and Breazeale's values

the Kerr constant values agree fairly closely with the values obtained from the depolarization data of Cabannes, while the discrepancies between these two sets and the values calculated from the depolarization data of Ananthakrishnan are greater, most of the difference being due to the latter's very low value of Δ for ethane. Both the depolarization measurement and the Kerr effect measurement are difficult for the small effects concerned; however the fair agreement between the depolarization data of Cabannes and the independent determinations of the Kerr constant by Stuart and Breazeale lead one to believe the Ananthakrishnan measurements to be in error.

Part III: Absolute configurations of several organic compounds on the basis of Kirkwood's polarizability theory

Several more or less obvious features of equation (125) which affect its use in discussing absolute configurations may first be mentioned. It applies only to molecules composed of groups each having an axis of optical symmetry. The polarizability theory is of course not restricted in principle to such molecules, but in practice this limitation exists because of the paucity of our knowledge concerning the optical properties of the groups. Evidently $g^{(o)}$ as given by equation (125) vanishes for interactions involving

isotropic groups - for such groups the higher approximations considered by Boys and de Mallemann must be used. Even if the groups are anisotropic, $g^{(o)}$ vanishes if all pairs of groups have their optical axes coplanar with the line joining the group centers, for in this case the triple scalar product appearing in equation (125) vanishes. Furthermore, this will also be true if in the case of free rotation around valence bonds the coplanarity of the three lines holds on the average. Thus for such compounds as CHClBrI, where all substituent groups to a first approximation would be treated as having the directions of their bonds as cylindrical axes of symmetry, $g^{(o)}$ will vanish in the first order. It is possible that the interactions with the central carbon atom might result in distortion of the symmetry of the groups, and so give rise to a nonvanishing $g^{(o)}$. The higher order polarizability terms of de Mallemann and Boys do not vanish for such molecules, and would therefore make some contributions to $g^{(o)}$. The compound cited has not been resolved, so that its rotation is not known.

In considering the application of the theory to specific substances, the points just mentioned must be kept in mind, as well as the fact that resonance between substituent groups is forbidden. The approximations involved are expected to become worse as the size of the individual groups relative to that of the whole molecule increases, so that the smaller the groups the better the approximation. Furthermore,

it seems desirable to assign configurations to several different molecules which can be configurationally related by the ordinary techniques of the organic chemist, thus affording a check of the theory (assuming the interpretations of the organic chemist to be correct). If this is to be done, some attention must be paid to selecting compounds which can be conveniently resolved, etc. The various requirements are not easily satisfied simultaneously, so that fewer compounds are suitable than might be expected.

Besides the features discussed, the calculation of $g^{(o)}$ as given by equation (125) requires a knowledge of the structure of the molecule. The term is not in general greatly sensitive to small changes in bond distances and bond angles in the molecule, so that in the majority of cases the normal covalent bond radii, and tetrahedral or near-tetrahedral geometry of the carbon atoms may be assumed. However in mulecules having internal rotations which change the relative orientation of one or more pairs of substituent groups, the optical activity will often be found to depend critically on the conformation with respect to this degree of freedom (actually often being of different sign for various orientations, and averaging to zero in the case of free rotation; see above). In such compounds rather precise information may be required concerning the internal conformation in order to make unequivocal calculations. Because usually

several different orientations with respect to the internal rotation will correspond to positions of stable equilibrium, and because these may correspond to different potential energies and contribute unequally to the rotatory power, strong temperature dependence of the latter may result. Conversely, rigid molecules (i.e., those having no low frequency internal rotational degrees of freedom) would be expected to have specific rotations depending only on the temperature through variations of the density and therefore the refractive index.

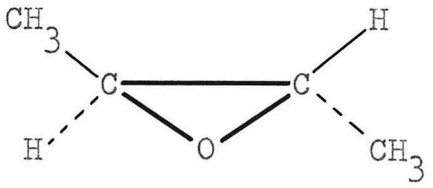
The compounds selected for application of the $g^{(o)}$ theory in the present series of researches are trans-2,3-epoxybutane, 1,2-dibromopropane and 1,2-dichloropropane. The first of these seemed desirable since the nuclear framework is presumably nearly rigid, except for the rotation of the methyl groups, and since the molecular structure had been previously investigated by Brockway and Cross[39] using the electron diffraction method. Furthermore, the relative configurational studies of Lucas and Garner[40] relate the configurations of the compound in the D and L series, so that an assignment of absolute configuration to trans-2,3-epoxybutane results in an assignment for the members of the whole series. The other two compounds have internal rotational degrees of freedom which may be expected to have a profound influence on their optical activity. An electron diffraction investigation of the molecular structure of 1,2-dichloropropane

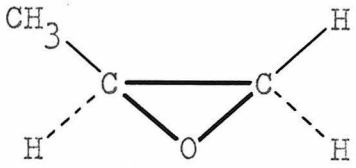
is to be described in Section V of this thesis. The structure of 1,2-dibromopropane had been previously investigated by Schomaker and Stevenson[41], again by electron diffraction.

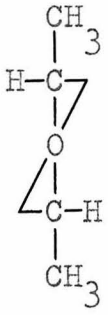
trans-2,3-Epoxybutane

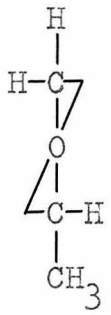
The spatial configuration for which the calculations have been performed is indicated in Figure 1. Inasmuch as we will have occasion to refer to the related compound propylene oxide, it is also shown. In the figure the heavy solid lines lie in the plane of the paper; the light solid lines project above the paper toward the reader; the dotted lines project below the paper away from the reader. Also shown in Figure 1 are the projection formulas of these enantiomorphs according to the projection convention of Fischer[43].

The prescription for obtaining these projections from a three dimensional model is the following: the main carbon chain of the molecule is arranged so that it lies in a plane and so that each carbon-carbon bond is cis with respect to both of its next-but-one neighbors. The carbon-carbon chain is then imagined to be straightened out by the bending of each C-C-C bond angle of the chain, the relative orientation of three of the bonds of each of the chain carbon atoms being preserved in the process. The straightened chain is then laid in the plane of the paper and rotated about its axis until all the substituent groups are oriented towards the reader, away from the plane of the paper. The structure is now projected onto the paper. In this way a unique correlation between









trans-2,3-Epoxybutane

$|[\alpha]_D| = 59°$

Propylene oxide

$|[\alpha]_D| = 13°$

Figure 1

Top, absolute configurations to which the discussion in the text applies; bottom, the projection formulas of these isomers according to the Fischer projection convention. Fischer's assumption for the absolute configuration of glucose assigns these configurations to the levorotatory isomers. Independent of any assumptions about absolute configuration, the relative configurational studies show these two isomers to have specific rotations of the same sign. The calculations in this thesis assign these configurations to the levorotatory isomers.

spatial configuration and a two dimensional formula is obtained. Although not essential to the latter, with some classes of compounds certain orientations of the two dimensional formulas have become customary; for instance, with the sugars the planar formula if written with the chain vertical is oriented so that the more highly oxidized end of the molecule is on top.

There is a second convention due to Fischer, to be sharply distinguished from the projection convention just described, which relates to the absolute configuration of optically active compounds. Lacking a solution to the latter problem, Fischer[43] for convenience assumed dextrorotatory glucose to have the configuration implied by the projection formula shown in Figure 2. This assumption, coupled with the relative configurational studies of organic chemistry, results in assignments of absolute configuration to a large number of substances. In particular the work of Lucas and Garner[40] for 2,3-epoxybutane and the experimental work of Levene and Walti[42] on propylene oxide as reinterpreted on the basis of modern configurational knowledge result in the assignment of the absolute configurations of Figure 1 to the levorotatory isomers of both these compounds, on the basis of Fischer's absolute configuration assumption. Apart from the latter, and of importance for our later discussion, the significance of the relative configurational investigations may be stated in more geometrical

terms as follows: the replacement of either methyl group of a given enantiomorph of trans-2,3-epoxybutane without inversion gives the enantiomorph of propylene oxide having the same sign of rotation.

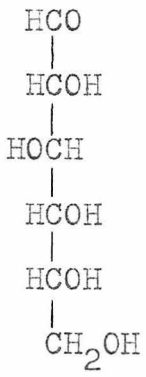


Figure 2. Dextrorotatory glucose, according to the Fischer projection convention and the Fischer absolute configuration assumption.

The magnitudes of specific rotations given in Figure 1 are for the pure liquids at 25° C. As will be clear from the discussion of Section I, the theory applies most rigorously to dilute vapors. Specific rotations in the vapor are not available; however Fickett[44] has made a rough measurement of the rotation of the epoxybutane in 2% heptane solution, finding a change of only a degree or so in the specific rotation. This is what the theory of Section I would predict if recklessly applied to the liquid and solution measurements, inasmuch as through a coincidence 2,3-epoxybutane and heptane have nearly identical indices of refraction. Apart from this, the constancy of the specific rotation upon solution indicates that no special liquid effects are acting in 2,3-epoxybutane, and presumably none in propylene oxide.

The structural parameters of interest here as reported by Brockway and Cross[39] are 1.54 Å for the carbon-carbon bonds, $57^{\circ}26'$ for the ring carbon-carbon-oxygen angles, and $125^{\circ}10'$ for all the other bond angles of the ring carbon atoms.

The first step, and a very important one, in applying the polarizability theory is the decomposition of the molecule into groups. The structure of the theory as formulated by Kirkwood assigns a special role to a central group, to which all the other groups (called substituent groups) are bonded, there being no bonding or electron exchange of other kinds between any of the substituent groups. As a consequence of this formulation of the theory, groups such as a chlorine bonded to an asymmetric carbon may be treated as having anisotropic polarizability ellipsoids due to the interaction with the asymmetric carbon atoms. It is however possible to construct the theory in an alternative manner, in which the molecule is considered as composed of N + 1 groups of atoms, between which in the zero-order approximation no interactions occur - i.e., there is no central group specially considered. The first-order perturbation is then taken, as before, as the dipole-dipole potential energy of interaction of pairs of groups all of which are now considered, whereas previously no pairs involving the central group appeared in the perturbation, inasmuch as such terms were assumed to be included in the zero-order Hamiltonian. The

analysis proceeds in exactly the same manner as before, the only change in the final result being that in equation (125) all groups are included in summing over the pairs. This procedure would be unsatisfactory for the purposes of the first-order $g^{(o)}$ theory in the case of a group such as our previous example of a chlorine atom, as such a group would be isotropic in this approximation, and in general this method would be expected to be less accurate than that used by Kirkwood. However, it might occasionally be more convenient and also reasonably satisfactory in case all the groups have appreciable intrinsic anisotropy.

In the case of the epoxybutane, perhaps the most obvious division into groups is that in which the carbon-oxygen ring with the two attached hydrogens is treated as the central group, the two methyl groups being considered as substituents. Equation (125) then gives $g^{(o)}$ as a single term involving the methyl-methyl interaction. Using the same scheme for propylene oxide, the central group is the same as before, while $g^{(o)}$ is given as a term involving the interactions of the methyl groups with the <u>trans</u> hydrogen. The other hydrogens bonded to the ring could in both cases be considered as separate constituent groups; however if they are treated as cylindrically symmetrical around their bonds, and the methyl groups similarly, it is readily seen that if the Brockway and Cross assumption of all bond angles outside the ring on the middle carbon atom being equal is

correct, then all the interactions of these other hydrogens with a methyl group or with the hydrogen trans with respect to the methyl group vanish. Even if small deviations from the Brockway-Cross values for the angles occur, the terms would still be expected to be small. The only nonvanishing term involving these other two hydrogens is then the interaction of one with the other. This also would be expected to be small, considering the small polarizability of hydrogen unless it should have an anisotropy ratio approaching the maximum value of three, which seems unlikely. On the basis of this scheme of subdivision, the smallness of the contributions of hydrogen terms to $g^{(0)}$ is supported by comparison of the magnitudes of the rotations of the two compounds under discussion.

The subdivision just described, although relatively simple in principle, has the disadvantage that relatively little is known of the optical properties of a methyl group bonded to this central group. Inasmuch as the latter has a relatively large dipole moment, and also because of the strains involved in the bonds of the ring carbons, it might be expected that the cylindrical symmetry of the methyl group would be somewhat distorted, as well as possibly some alteration in the value of the anisotropy ration, even if the first effect should be small. Indeed it will be seen from the calculations below that use of optical parameters for the methyl group derived from the experimental data for ethane

fall rather short of reproducing the experimental rotatory power of 2,3-epoxybutane, the calculated value being approximately one-third to one-quarter the observed.

It is also possible to proceed in the alternative version of the theory described previously. Abandoning the designation of a special central group, we may consider the molecules as composed of a methyl group or groups, the carbon-oxygen ring with two attached hydrogens, and in the case of propylene oxide the third hydrogen atom may be considered as another group. In the zero-order approximation appropriate to the present discussion, however, the hydrogen will be isotropic and so not contribute to the first-order optical rotatory power. Under this scheme, the optical activity of 2,3-epoxybutane will appear as the sum of three terms, a methyl-methyl interaction and two methyl-ring interactions. It is readily seen, because of the twofold axis of symmetry of 2,3-epoxybutane, that the latter two are completely equivalent; furthermore, if in propylene oxide the bond angles of the ring carbon to which the methyl group is attached are the same as those in 2,3-epoxybutane, then each methyl-ring interaction in the latter compound contributes algebraically the same rotation as the single similar interaction in propylene oxide. But with the present subdivision in the latter compound, its rotatory power is due to the single methyl-ring interaction.

It may be here mentioned that although we have been considering the carbon-oxygen ring and the attached hydrogens

as comprising a group, there is no necessity of doing so - we can, if we like, consider each atom as a group. The advantage of doing the latter has been previously mentioned; namely, the $g^{(o)}$ approximation becomes increasingly better the smaller the size of the groups compared to the molecular dimensions. Opposing this advantage, however, is the disadvantage that as we decompose large groups into smaller ones, the structure of the theory forces us to neglect more and more bonding interactions in the zero-order approximation. Put in other words, if we eventually decide to consider each atom of the molecule as a separate group, then we have to neglect in our zero-order wave functions all interactions between the atoms. The groups then become isotropic, and we have reduced the problem to the one considered by Boys. It seems likely that an intermediate procedure is preferable.

It is probably not an adequate approximation to consider the carbon-oxygen ring as cylindrically symmetrical, so that the calculation of the principal polarizabilities requires knowledge of both the Kerr constant and the degree of depolarization of scattered light. The latter is not available; the term as a result eludes calculation at the present time. The argument of the preceding paragraph shows, however, how the experimental value for the rotatory power of propylene oxide may be used to estimate the methyl-ring term; in this way we obtain a quasi-experimental value of 33° as the magnitude of the methyl-methyl contribution to the specific rotation of 2,3-epoxybutane.

In calculating theoretically this last interaction using equation (125), the structural data of Brockway and Cross have been used, the methyl groups being treated as cylindrically symmetrical about their bonds, with their centers at their carbon atoms. For the isomer of Figure 1, use of the value $\beta = 0.35$ for the anisotropy of the methyl groups leads to the value $[\alpha]_D = -17^\circ$ for the contribution of the methyl-methyl interaction for a medium of refractive index 1.37, corresponding approximately to that of both the pure liquid and the dilute heptane solution. The magnitude is roughly one-half the "experimental" value; the discrepancy may be due to use of too small an anisotropy ratio, or to distortion of the polarizability ellipsoids. It seems unlikely that the error could be so large as to result in the wrong sign.

The calculation just described results in the assignment of the configuration given in Figure 1 to the levorotatory isomer of trans-2,3-epoxybutane, thus verifying the Fischer convention for the absolute configurations of the whole series of optically active compounds.

1,2-Dichloropropane (Propylene chloride)

The configuration to which the calculations to be described will apply is shown in Figure 3, where the carbon-chlorine bond of the $-CH_2Cl$ group, the 1,2 carbon-carbon bond, and the dotted line through C_2 lie in the plane of the paper. The internal rotation around the 1,2 carbon-carbon

bond will be shown to have a profound effect on the optical activity; as the coordinate specifying this degree of freedom we choose the angle between the two planes formed by the 1,2 carbon-carbon bond with the two carbon-chlorine bonds. The angle is called φ and is taken as zero when the two chlorines are <u>trans</u> with respect to each other. The positive direction of rotation from the <u>trans</u> position is taken as that which brings the methyl group into the <u>cis</u> position with respect to the chlorine bonded to C_1. Put otherwise, the positive direction of φ corresponds to clockwise rotation of the $-CH(CH_3)Cl$ group relative to the $-CH_2Cl$ group when viewed along the 1,2 carbon-carbon bond looking from C_1 towards C_2. When φ is zero, the chlorines being <u>trans</u>, then the methyl group projects towards the reader, away from the plane of the paper. In Figure 3 the projection formula of the same isomer is also shown according to the convention of Fischer.

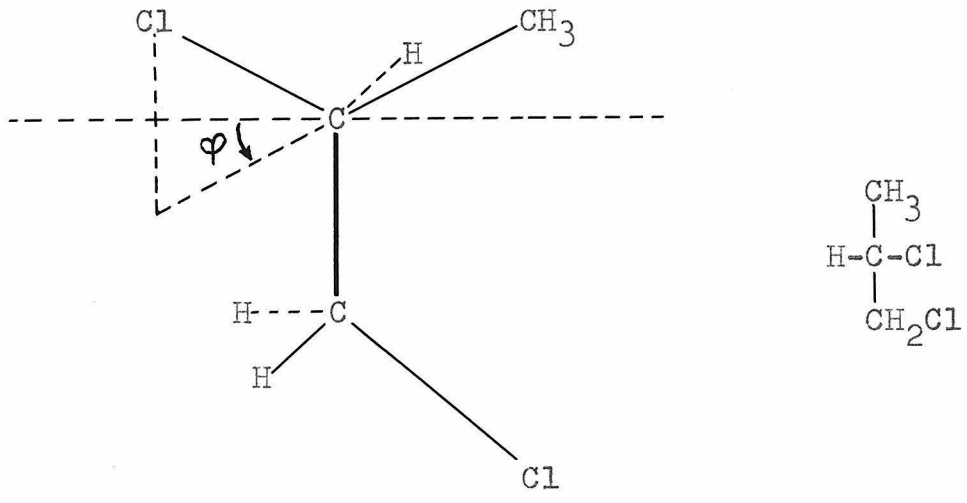


Figure 3 1,2-Dichloropropane
Left, the enantiomorph to which the calculations apply; right, the projection formula of this isomer, according to the Fischer projection convention.

In applying equation (125) to the calculation of the rotatory power of propylene chloride, the molecule has been considered as being composed of the three substituent groups $-CH_2Cl$, $-Cl$, and $-CH_3$, with the asymmetric carbon atom playing the role of the central group. The terms involving the hydrogen bonded to the latter have been neglected, as they may be supposed small compared to the others. The chlorine atom and the methyl group were considered cylindrically symmetrical about their bonds to the asymmetric carbon, while the $-CH_2Cl$ group was treated as cylindrically symmetrical around the carbon-chlorine bond axis, in accordance with the procedure described earlier for groups having large intrinsic anisotropy. The optical center of the chlorine atom was taken at its nucleus, that of the methyl group at the nucleus of its carbon atom, while the center of the $-CH_2Cl$ group was placed at the center of mass of its carbon and chlorine atoms.

As has been previously indicated, the optical activity depends critically on the internal angle φ. Considering the low frequencies and large moments of inertia involved in this internal degree of freedom, it is doubtless an adequate approximation to utilize classical statistical mechanical phase integrals rather than the quantum mechanical sums-over-states in performing the required averaging. Furthermore the discussion of Section V indicates that it will be a sufficient approximation to perform this averaging using as the weighting function the Boltzmann factor $exp\left(-V(\varphi)/kT\right)$, ($V(\varphi)$ being the potential energy restricting the internal rotation)

rather than using the rigorous (in the classical approximation) weighting function and integrating over all vibrational and rotational coordinates and the corresponding momenta. Adopting this approximation, we require the optical activity of the molecule as a function of the internal angle φ. In performing this calculation tetrahedral carbon bond angles were assumed, and the distances C-C = 1.54Å, C-Cl = 1.77Å used. These values are somewhat different than the values found in the electron diffraction investigation; however, inasmuch as the rotatory power does not depend critically on the exact values of these parameters it has not seemed worth-while to repeat the calculations.

The term contributed by the interaction of the methyl group and the chlorine atom bonded to the asymmetric carbon atom vanishes, so that only two terms need be calculated, namely, the Cl----CH_2Cl term and the CH_3---CH_2Cl term. The calculated specific rotation as a function of the internal angle is shown by the curves of Figure 4, for different values of the anisotropy ratios of the groups calculated from the experimental data of different investigators given in Table 2 of this section. A fourth curve is also shown, in which the anisotropy ratios derived from Cabannes' data were again used, the optical center of the -CH_2Cl group being taken at the chlorine nucleus. Comparison of this curve with the other one calculated from Cabannes' data illustrates how the optical activity depends only slightly on exact values of the distances. The curves of Figure 4 are computed for a medium of refractive index 1.44, the

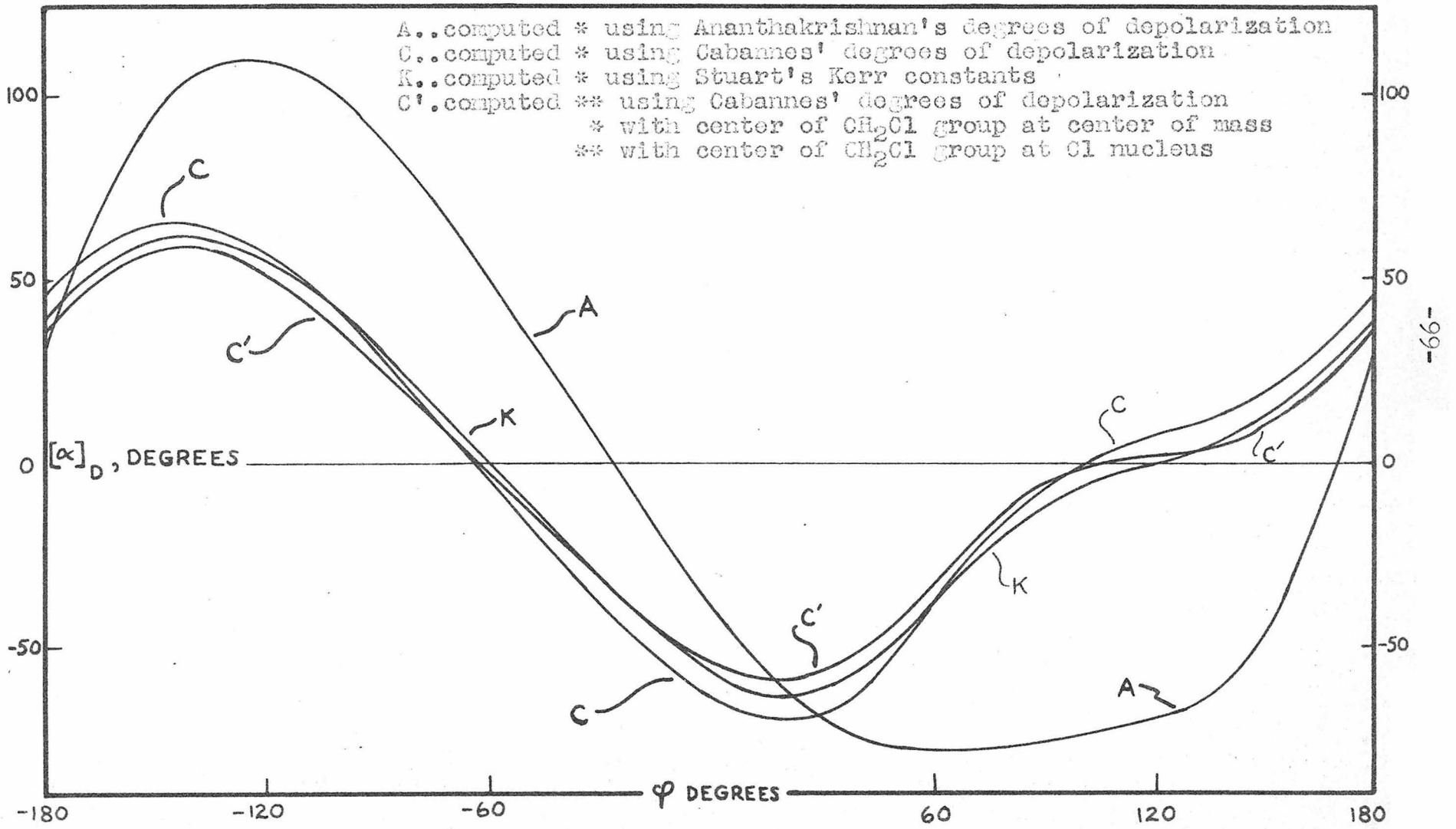


Figure 4. Specific rotation of the enantiomorph of 1,2-dichloropropane shown in Figure 3, as a function of the internal angle.

value corresponding to the pure liquid at room temperature.

For comparison with experimental values of the rotatory power and for assignments of absolute configuration, the average specific rotation must be computed, for which computation we need to know the functional dependence of the potential energy hindering rotation V (φ). For this purpose the electron diffraction investigation described in Section V of this thesis was undertaken. There recent dipole moment data for propylene chloride in the vapor state are also discussed and analyzed. The determination of V (φ) is there discussed at some length, particularly the range of variation of V (φ) within which satisfactory interpretations of the dipole moment and electron diffraction data may be obtained. Tables 6 and 7 in that section also give the average specific rotation computed from curves C or C' of Figure 4 for a variety of potentials in the aforementioned range. Here the discussion will be limited to a statement of the general features of the problem and to the results obtained.

Three positions of stable equilibrium with respect to rotations around the 1,2 carbon-carbon bond would be expected, corresponding to the three nonequivalent conformations in which the bonds of C_1 and C_2 are staggered, i.e., in the neighborhood of $\varphi = 0, \pm 2\pi/3$. There is no symmetry requiring the minima to occur at exactly these angles; indeed, it seems likely that steric forces will displace the minima somewhat. Of these three, the one with $\varphi = 2\pi/3$

is expected because of steric effects to be of sufficiently high energy relative to the other two so as to be of negligible importance at temperatures of interest here. Of the other two minima the one near $\varphi = 0$, which we shall call the trans minima, is expected to be of lower energy, by analogy with other compounds and as proven by the discussion of Section V. However, the minimum near $\varphi = -2\pi/3$, designated as the gauche or skew minimum, is expected to be of appreciable significance by comparison with the related compounds ethylene chloride and 1,1,2-trichloroethane, as discussed in Section V.

From Figure 4 it is evident that the contributions of these two conformations to the optical activity will very likely be opposite in sign. Furthermore, the exact position of the trans minimum is uncertain, inasmuch as the structure investigations can only be interpreted safely as requiring it to lie in a range of twenty-five to thirty degrees either side of $\varphi = 0$. Steric repulsions between the methyl group and the chlorine bonded to C_1 may become effective in the neighborhood of $\varphi = 0$, tending to give a potential minimum displaced slightly from $\varphi = 0$ towards negative values of φ. The possibility arises that this displacement, which carries the trans potential energy minimum toward the node of the computed specific rotation curve, combined with a sufficiently large contribution of the skew minimum may result in the sign of the average rotation being opposite to that of the trans minimum. However, it is found, when the averaging is done with curve C of Figure 4 at $T = 300^{\circ}$ K, that all potentials which are satisfactory for the interpretation of the

dipole moment and electron diffraction data result in giving a negative specific rotation for the isomer of Figure 3, of the general order of magnitude of -20 deg./dm., the range of values being approximately -10 to -50 deg./dm. On the other hand, if curve A of Figure 4 is used, the sign of the specific rotation is not determined by the range of potentials acceptable on the basis of the aforementioned criteria, so that no conclusions regarding absolute configuration can be drawn from comparison with experimental rotations at this single temperature.

It is however interesting to point out that measurement of the temperature dependence of the optical activity will make possible an assignment of absolute configuration with only the two assumptions that, as indicated by Figure 4, the specific rotation of the skew isomer is algebraically greater that that of the trans isomer, and that the sign of the rotation computed for the skew isomer is correct.

Suppose, for example, that the magnitude of $[\alpha]_D/n^2+3$ increases on raising the temperature. It then follows that the sign of the contribution of the skew isomer to the optical activity is the same as that of the average rotation in the temperature range in question. Our assumption is that the former is correctly determined by the theory as being associated with a definite one of the two isomers. Consequently the experiment permits an assignment of absolute configuration to the two antipodes: if the magnitude of

$[\alpha]/n^2+3$ increases with raise of temperature then the dextrorotatory isomer has the configuration of Figure 3; if this quantity decreases with rising temperature, the levorotatory isomer has this configuration. It is desirable that these measurements be carried out in the vapor state, as only in this case can the theory lay claim to rigor.

If the Ananthakrishnan measurements could be completely discounted, the configuration of Figure 3 could be assigned to levorotatory propylene chloride without reference to measurements at different temperatures, although the latter would of course be a valuable check. This assignment may be regarded as quite probable, but must be considered tentative until confirmed by the temperature dependence.

Propylene chloride has not been resolved; this problem, along with the determination of the relative configuration, is being attacked by Mr. Wildon Fickett under the direction of Professor Lucas. When this work is brought to a successful conclusion, particularly if it proves possible to measure the temperature dependence of the rotation in the vapor, then a check of the theory will be afforded by the comparison of the resulting assignments of configuration.

1,2-Dibromopropane (Propylene bromide)

The isomer to which the discussion will apply is that of Figure 3 with the chlorines replaced by bromines. With the same subdivisions of groups, the same assumptions as regards the symmetry of the latter, and so forth, as for

propylene chloride, the curves of Figure 5 were calculated using the anisotropies given in Table 2, for a medium of refractive index 1.52, this value corresponding to that of the pure liquid. The curves are similar to those for propylene chloride, an important difference however being that with propylene bromide the node of the curve is closer to the conformation $\varphi = 0$.

The electron diffraction investigation of Schomaker and Stevenson[41] did not consider explicitly the possible existence of potential minima other than trans, nor in detail the possible variations of the trans equilibrium position from $\varphi = 0$. Furthermore, no vapor dipole moment data (or even solution measurements over a temperature range) have been published, so that practically no information is available concerning $V(\varphi)$ for propylene bromide. However by analogy with the results of Gwinn and Pitzer[45] for ethylene chloride and bromide, a smaller amount of the skew conformation would be expected in propylene bromide than in propylene chloride, so that we might expect to obtain an upper limit (algebraically) for the optical activity of the isomer of propylene bromide under discussion by using the potentials which were found satisfactory for the chloride. Calculations of this sort using curve K of Figure 5 again result in a uniformly negative sign for the specific rotation, but some values are quite close to zero, the range of values of $[\alpha]_D$ being roughly -2 to -25 deg./dm. The calculation does not therefore assure

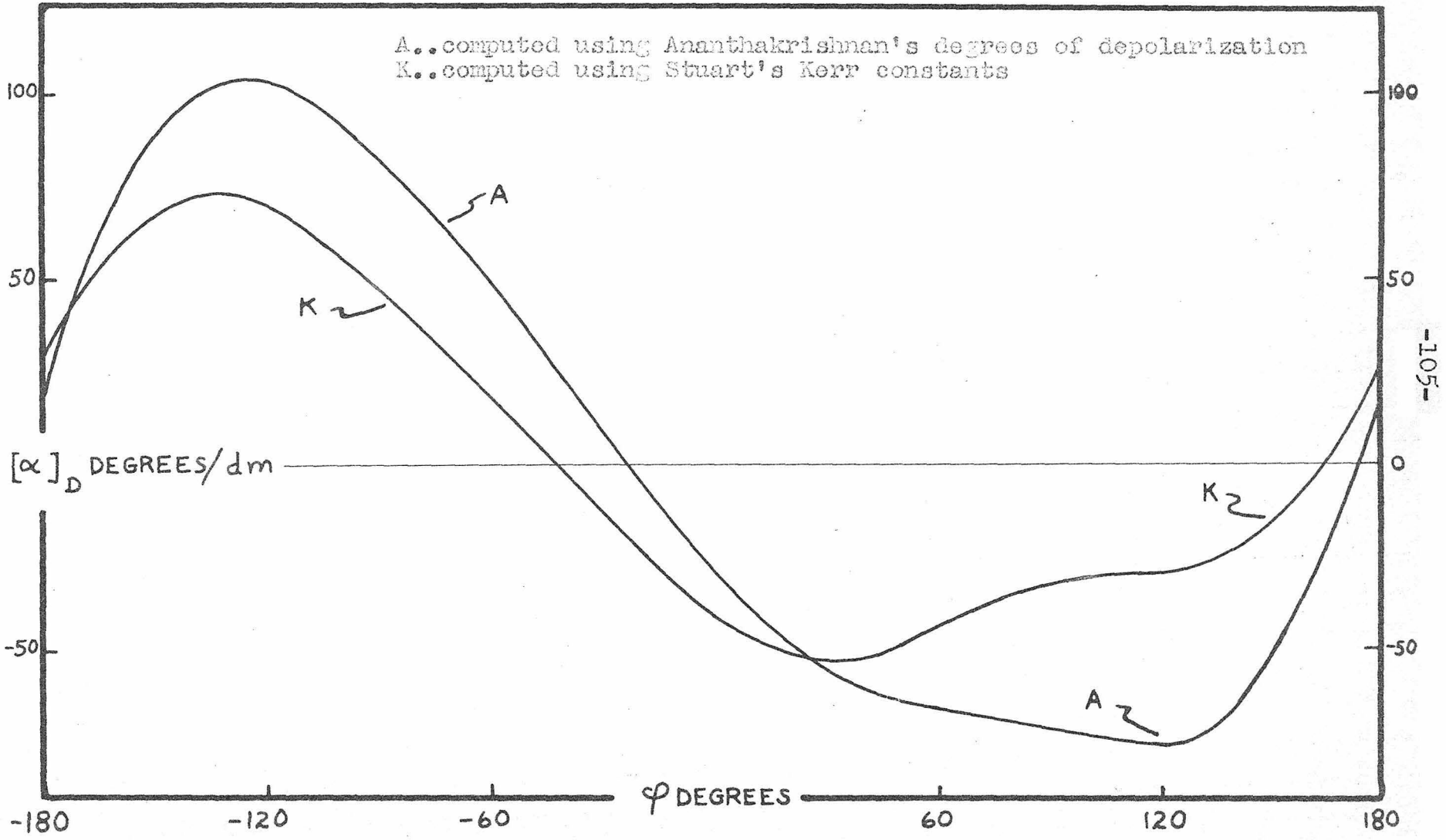


Figure 5. Specific rotation of the enantiomorph of 1,2-dibromopropane shown in Figure 3, as a function of the internal angle.

levorotation even using curve K. Thus the absolute configuration of propylene bromide is even less certain than that of propylene chloride on the basis of similar calculations.

Here again, however, measurement of the temperature dependence of $[\alpha]_D$ will afford a remedy to the situation, and make possible an assignment of absolute configuration to the isomers of propylene bromide. The relative configurational study of this compound is being carried out by Mr. Fickett and Professor Lucas along with the previously mentioned work on propylene chloride.

SECTION IV

OTHER THEORIES OF OPTICAL ACTIVITY

Part I Kuhn's application of the coupled oscillator theory to sec-butyl alcohol

We include this brief discussion of W. Kuhn's[46] use of the classical coupled oscillator theory in this section, although it is rather similar to the polarizability theories discussed in the preceding section.

The isomer considered by Kuhn is shown in Figure 6,

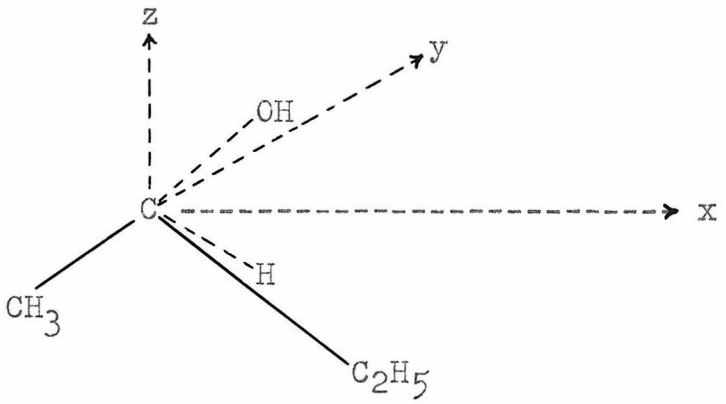


Figure 6. Levorotatory sec-butyl alcohol according to Kuhn.

where the CH_3 and C_2H_5 groups project toward the reader, the H and OH groups away from the reader (behind the plane of the paper). The x and z axes lie in the plane of the paper while the y axis is perpendicular to the latter, the positive direction pointing away from the reader. The carbon atom of the CH_3 group and the secondary carbon atom of the C_2H_5 group are

in the xy plane; the oxygen of the hydroxyl group and the hydrogen bonded to C* are in the yz plane.

Kuhn assumes the methyl and ethyl groups as well as the asymmetric carbon atom to be isotropic per se, becoming anisotropic through the interactions of the moments induced in them in the Silberstein manner. The hydroxyl group is taken to be anisotropic per se, with the principal axes u_1 parallel to the x axis, u_2 along the C-O bond and u_3 in the yz plane. The hydrogen bonded to the asymmetric carbon is neglected. He supposes the "sterically preferred" orientation of the hydroxyl group to be that in which it lies in the yz plane, and gives arguments to show that the plane determined by C* and OH (under his structural assumption, the yz plane) would be expected to contain the direction of greatest polarizability (Silberstein argument), and further that this last-mentioned direction would be the direction of vibration of the induced moment in the absorption band of longest wave length. It is the rotatory contribution of this band which he calculates, supposing it to dominate the rotatory power in the visible spectrum, a fact which he claims is supported by an analysis[47] of experimental rotatory dispersion data; this however is disputed by Levene and Rothen[48].

In computing the interactions of the induced moments in the C, CH_3, C_2H_5 and OH groups Kuhn considers only terms involving pairs of groups bonded to each other; for these he

uses the potential energy of dipole-dipole interaction. The theory is entirely similar in principle to the polarizability theory of de Mallemann involving the interaction of three groups one of which is anisotropic, the only difference being the restriction of the calculations to the contribution of a single absorption band rather than summing over all absorption bands. It is found with Kuhn's assumptions concerning the principal axes that the rotatory contribution of the normal mode u_2 (so called because it reduces to the u_2 mode of the hydroxyl group in the absence of the interactions with the other groups) vanishes, while the u_3 mode contributes levorotation, the u_1 mode dextrorotation. Under the above-mentioned assumptions it follows that the molecule of Figure 6 should have a levorotatory contribution from the absorption band nearest the visible; supposing this band to determine the sign of the rotation in the visible, the enantiomorph shown should be levorotatory.

Two major objections to the analysis of Kuhn suggest themselves, the first being the treatment of the ethyl and methyl groups as isotropic. Kuhn supports this assumption by citing the fact that the sign of the rotation does not change in replacing the ethyl group by such groups as the cyclohexyl or propyl groups. A second objection is that it is not at all clear that the orientation of the OH group assumed by Kuhn actually corresponds to the most stable position of equilibrium. Inasmuch as other equilibrium

positions are probably at least as important, and because the sign of the calculated rotation depends on the orientation assumed, it seems clear that the result should be regarded as open to some question. This point will be discussed at somewhat greater length when we take up the Eyring theory in the next part of this section.

The configuration found by Kuhn for levorotatory sec-butyl alcohol is the same as that obtained from relative configurational studies[43] combined with the absolute configuration of dextrorotatory glucose assigned by Fischer[43] on a postulatory basis. Thus the projection formula of the isomer of Figure 6 according to Fischer's projection convention is shown in Figure 7; it will be recognized as the usual formula for levorotatory sec-butyl alcohol.

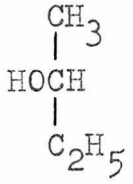


Figure 7 Levorotatory sec-butyl alcohol, as postulated by Fischer and calculated by Kuhn. Projection formula according to Fischer convention

Part II The one-electron theory of Eyring, et al.

The polarizability theories previously described and the Kuhn theory are to be regarded as derivatives of the Born coupled oscillator optical activity theory. The theory

developed by Eyring and his co-workers attributes the optical rotatory power to the motion of a single oscillator (electron) in a suitably asymmetric potential field. This idea (the basis of Drude's[9] previously mentioned model, later shown erroneous by Kuhn[10]) was for some time believed to be without foundation, inasmuch as in the reference quoted Kuhn purported to prove that a single oscillator could not show optical activity. Since the original paper of Condon, Altar and Eyring[22], however, Kuhn[47] has noted that his proof requires the assumption of only infinitesimal displacements; with the finite displacements implicit in quantum mechanical theory optical activity can be produced by the motion of a single oscillator in an asymmetric potential field. The contributions of such terms to the optical rotation are included in the g_k terms of equation (112) in Kirkwood's breakdown of the Rosenfeld formula in terms of the groups composing the molecule.

The procedure adopted by the Eyring school is similar in one respect to that of Kuhn in that instead of calculating the complete rotatory parameter g_k of a given group, only the contributions from one or more of the ultraviolet absorption bands lying closest to the visible are calculated, it being supposed that their rotatory contributions predominate in the optical activity observed in the visible region. It is further supposed that transitions responsible for these bands may

be adequately represented in terms of "one-electron transitions", i.e., that the upper and lower quantum states in question may be represented by wave functions having the form

$$\Psi_o = \varphi_o \psi_o$$

$$\Psi_n = \varphi_o \psi_n \quad ; \tag{135}$$

here Ψ_o and Ψ_n are the molecular wave functions for the lower and upper levels, respectively; ψ_o and ψ_n are the wave functions of the electron, one or more of whose transitions are assumed to account for the absorption band in question; φ_o is the wave function for the other electrons of the molecule, idealized as being the same in both upper and lower states.

Under these conditions the contribution $g_k\ (o \rightarrow n)$ of the absorption band in question to g_k, where k denotes the chromophoric group, reduces to

$$g_k(o \rightarrow n) = \frac{c}{3\pi h} \frac{Im\{\vec{\mu}_{on} \cdot \vec{m}_{no}\}}{\nu_{no}^2 - \nu^2} \quad , \tag{136}$$

where $\vec{\mu}$ and $\vec{m}$ are now the dipole moment and magnetic operators

of the chromophoric electrons, the matrix elements being taken with the wave functions ψ_o and ψ_n of equation (135). The g_k of the other groups, as well as $g^{(o)}$ and $g^{(1)}$ vanish in this approximation. It may however be mentioned that while the approximation of neglecting the change of quantum state of the other electrons with the transition of the chromophoric electron may not be serious for the purpose of calculating the one-electron rotatory power, the vanishing of $g^{(o)}$ and $g^{(1)}$ upon its introduction in no way demonstrates that these terms are really negligible.

The problem now reduces itself to the computation of the wave functions ψ_o and ψ_n for the chromophoric electron, and the evaluation of the matrix elements appearing in equation (136). Different procedures are possible in obtaining approximations to the wave functions, and it will be simplest for the purpose of the present discussion to outline the method used by Gorin, Walter and Eyring[29] for the specific case of sec-butyl alcohol.

For this molecule it is assumed with Kuhn that the optical activity is due to the absorption band of the hydroxyl group lying nearest the visible. This band is attributed to transitions of a nonbonding electron on the oxygen atom. The wave functions of this chromophoric electron are taken to be solutions of the Hartree equation

$$\nabla^2\psi + \frac{h^2}{8\pi^2 m}\left\{E - V(r) - \sum_s \sum_i{}^{(s)} e^2 \int \frac{\varphi_{is}^2\, d\tau_i}{r_{is}} + \sum_s \frac{z_s e^2}{r_s}\right\}\psi = 0. \qquad (137)$$

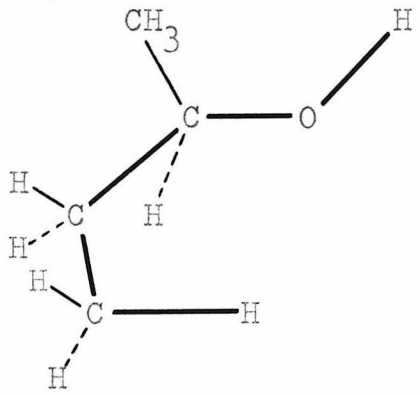
V(r) represents the potential energy of the chromophoric electron due to the oxygen nucleus and electrons, and is taken as hydrogen-like with effective nuclear charges for the various levels which give the empirical ionization and resonance potentials for the given molecule or a related one. The first sum, with dummy index s, is over the other nuclei of the molecule. The second sum is over the electrons associated with nucleus s. The wave function φ_{is} is that of the electron i associated with nucleus s, while r_{is} is the distance between the chromophoric electron and electron i. The double sum is thus the potential energy of the chromophoric electron in the field of the other electrons in the Hartree approximation.

The last term is the potential energy of the chromophoric electron in the field of the other nuclei of the molecule, z_s being the atomic number of nucleus s, r_s the distance of the chromophoric electron from this nucleus. Exchange is neglected, bonding electronic pairs being

assigned one each to the atoms forming the bond.

First-order perturbation theory is used, the last two terms within the brackets in equation (137) being treated as the perturbation. The zero-order wave functions for the chromophoric electron are thus ordinary hydrogen-like functions. It is readily seen that no optical activity is obtained in the zero-th order. In evaluating the integrals appearing in the perturbation terms, approximate screening constant wave functions are used for the electrons of the hydrogen and carbon atoms of the molecule.

The enantiomorph to which their calculations apply and the molecular structure assumed for it are shown in Figure 8, where the heavy lines are in the plane



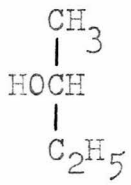


Figure 8. Left, calculated configuration and assumed molecular structure of levorotatory sec-butyl alcohol according to Gorin, Walter and Eyring. Right, projection formula of the isomer on the left according to the Fischer projection convention. The absolute configuration agrees with that deduced from Fischer's assumed absolute configuration of glucose.

of the paper, the dotted lines project away from the reader, the solid light lines toward the reader. The Fischer projection formula for this isomer is also shown.

The perturbation previously mentioned is subdivided into two parts, H' indicating that due to the carbon and hydrogen atoms bonded to the oxygen, H'' that due to all the other atoms. Because of the proximity of the atoms giving rise to H', this term is larger than H'', so that the latter can be neglected in comparison with the former except in those cases where symmetry results in a null contribution from H'. (H' is symmetric with respect to the C*-hydroxyl plane and of itself would not give rise to optical activity. H'' has no symmetry with respect to this plane.)

The zero-order ground state wave function of the chromophoric electron is taken as the hydrogen-like wave function ψ_{2px} with an appropriate effective atomic number; the y and z axes of the coordinate system are taken in the plane of the paper in Figure 8, the x axis perpendicular thereto. In this treatment the effect of the perturbation H'' on the ground state is ignored, so that only hydrogen-like functions odd with respect to the yz plane will appear in the expansion of the ground state in terms of the zero-order wave functions. The authors limit their calculations to the inclusion of only one such term, namely ψ_{3px}.

Three zero-order excited states are considered, namely ψ_{3s}, ψ_{3py} and ψ_{3pz}, it being supposed that the rotatory power

in the visible is dominated by the contributions of transitions to these excited states. These three states are degenerate in zeroth order; all are symmetric with respect to the yz plane, so that the degeneracy is removed by the perturbation H'. The correct set of zeroth order wave functions are then individually combined with the wave functions ψ_{2py}, ψ_{2pz}, ψ_{3dxz} and ψ_{3dxy} by means of the perturbation H' for the first two, by means of H'' for the last two, to give the first-order approximations to the three excited levels. It is the contributions of the last two wave functions, ψ_{3dxz} and ψ_{3dxy}, which remove the even symmetry character of the excited states with respect to the yz plane. Thus the initial state is odd with respect to this plane, while the final states are nearly even. With these symmetry characters of the initial and final states there arises the possibility of a large electric moment and a small magnetic moment matrix element perpendicular to the yz plane, as well as a small electric moment matrix element and a large magnetic moment matrix element in this plane. However with the wave functions selected by Gorin, Walter and Eyring for inclusion in the expansions of the ground and excited states, it is found that in these transitions the components of the magnetic moment perpendicular to the plane vanish, due to elements of symmetry common to this component of the operator and to the various zero-order wave functions utilized in the expansions of the ground and excited states.

For similar reasons the expected large magnetic moment in the yz plane fails to materialize, the magnetic moment in this direction being that due to the perturbation H'. The electric moment in this plane is found to be due to the perturbation H'', so that the term calculated by Gorin, Walter and Eyring is of the order H'H''.

With these assumptions the problem is reduced to the evaluation of the integrals involved. The procedure is lengthy though not particularly difficult, the integrals being amenable to analytical evaluation. For the configuration and conformtion of Figure 8 these authors calculated $g = -2.70 \times 10^{-35}$. The magnitude of g computed from the experimental rotation for the pure liquid is 1.4×10^{-35}. Gorin, Walter and Eyring also computed the rotation for the orientation in which the hydroxyl group in Figure 8 is turned into the position coplanar with the C*-H bond, finding for this orientation $g = -9.67 \times 10^{-35}$. They proposed these two conformations as being the orientations of greatest probability, supposing them to be stabilized by internal hydrogen bonding, and so concluded that the isomer of Figure 8 is levorotatory, thus verifying the absolute configuration assumed by Fischer for glucose.

Objections may be raised to the calculations of Gorin, Walter and Eyring at several points. It has not been convincingly demonstated that the sign of the total rotation in the visible is actually the same as the sign of the contributions of the absorption band for which the calculation is

carried out. Supposing this actually to be the case however the adequacy of the approximations made seem open to question. The success of first-order perturbation theory depends on the closeness of approximation of the zero-order wave functions; whether the perturbation calculation converges sufficiently rapidly when hydrogen-like wave functions are used for the latter is not demonstrated.

The effects of electron exchange are completely neglected in the calculation of the Hartree perturbing potentials due to the electron clouds of the surrounding atoms. Even supposing the approximations so far mentioned to be valid, omission of the state ψ_{3px} from consideration with the three other excited levels with the remark that "it would considerably complicate the calculation without giving an important contribution to the optical activity" seems questionable. This state is degenerate with the three excited states used by these authors. The perturbation H'' will combine it in the zeroth order with the three functions considered as excited states previously, and in the first order with such states as ψ_{2py} and ψ_{2pz} ; the perturbation H' will combine it in the first order with other odd (with respect to the yz plane) states such as ψ_{3dxz} and ψ_{3dxy} . Taking the same ground state as before, non-vanishing matrix elements for the electric and magnetic moments in the y z plane are found which result in a contribution to the optical activity of the same order H'H''

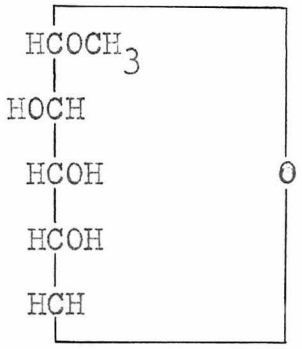
as found for these other states. There is no apparent reason why this contribution should be small compared to those previously calculated. If it is of the same order of magnitude, it might easily change the calculated sign. The omission of f and higher levels in the expansion of the excited state wave functions is also questionable, inasmuch as their inclusion (due to the perturbation H'') would result in components of the magnetic moment perpendicular to the plane in the transitions to the three excited states considered by Gorin, Walter and Eyring. These same excited states give an electric moment in this direction in the zeroth order, so that inclusion of such terms would give rise to a contribution to the optical activity of the order H''.

Finally, certain exceptions may be taken to the conformations assumed by Gorin, Walter and Eyring. The orientation of the hydroxyl group in Figure 8 probably corresponds to a potential energy minimum due to steric repulsions between the hydrogen of the hydroxyl and the groups bonded to C*. On the other hand, the orientation of the ethyl group with respect to its rotation around the 2,3-carbon-carbon bond is very likely unstable, the great weight of experimental evidence favoring the stability of staggered rather than eclipsed conformations in compounds having internal rotation, except where strong hydroxyl bonds may stabilize the eclipsed conformation. It is unlikely that hydrogen bonds involving hydrogens bonded to carbon will be sufficiently strong to

overcome the steric repulsions opposing the eclipsed orientations. The staggered conformation in which the ethyl group is rotated 180° from its position in Figure 8 would be expected to be approximately at a potential minimum. For the orientation of the hydroxyl group shown in Figure 8 the ethyl group makes no contribution to the rotatory power in either of these two positions in which its carbon atoms lie in the yz plane, in the approximations introduced by Gorin, Walter and Eyring. Thus their calculation may be considered as applying to the more stable conformation suggested. The second orientation considered by these authors in which the hydroxyl group, the asymmetric carbon and the latter's hydrogen are coplanar probably makes no appreciable contribution to the experimental rotation due to the instability of such eclipsed orientations. There are however two other orientations of the hydroxyl group which would be expected on the basis of modern structural knowledge to correspond to positions of stable equilibrium: first, that in which the hydrogen of the hydroxyl group is trans with respect to the methyl group bonded to C*; second, that in which it is trans with respect to the hydrogen bonded to C*. These were not considered by Gorin, Walter and Eyring; inasmuch as at least the first might be expected to have a statistical probability of the same order of magnitude as the original orientation considered by these authors, this omission serves to cast further doubt on the validity

of their calculations. Furthermore there are probably other stable orientations of the ethyl group which have statistical probabilities of the same order of magnitude as the one to which their treatment applies.

Calculations very similar to those just described for sec-butyl alcohol have been applied by Gorin, Kauzmann and Walter[30] to the sugars α-methylarabinopyranoside, β-methylarabinopyranoside, α-methyllyxopyranoside and β-methyllyxopyranoside. The calculations for α-methylarabinopyranoside were based on the enantiomorph shown in Figure 9, the conformation being the chair form in which the carbon-oxygen bonds of the hydroxyl groups attached to carbons 1, 2 and 3 are approximately perpendicular to the mean plane of the ring, rather than the other chair form in which these bonds are approximately in the mean plane of the ring. In the structural formula the two heavy lines lie in



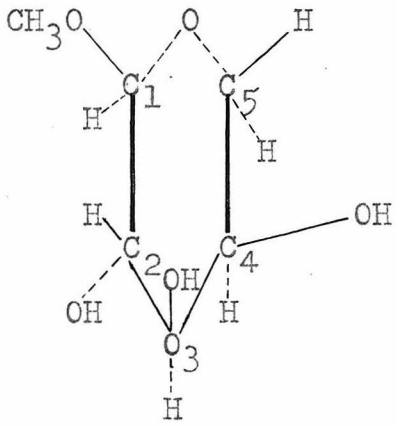
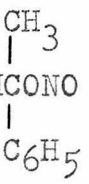


Figure 9. Fischer projection formula of levorotatory α-methylarabinopyranoside, as calculated by Gorin, Kauzmann and Walter, agreeing with that derived by relative configurational studies from the absolute configuration assumed by Fischer for glucose. The conformation to which their calculations apply is also shown.

the plane of the paper, the light solid lines project upwards toward the reader, the dotted lines downward. No attempt is made to indicate the orientations with respect to the internal rotations of the hydroxyl and methoxy groups, for which reference may be made to the original paper. Gorin, Kauzmann and Walter calculated $g = -1.06 \times 10^{-34}$ (observed $|g| = 0.46 \times 10^{-34}$) for this isomer. The projection formula of Figure 9 is in fact the one assigned to the levorotatory isomer of this sugar, thus again supporting the correctness of the original assumption of Fischer. The agreement between the calculation for this sugar and that for sec-butyl alcohol in this respect is a support for the one-electron theory in that a disagreement on this point (i.e., finding agreement with the Fischer assumption in one case, disagreement in another) would be embarassing. Such agreement of course does not prove the calculations are valid, particularly in the face of the objections made above. Similar agreement with the relative configurational studies of organic chemistry was found by Gorin, Kauzmann and Walter among all four of the sugars they investigated.

The one-electron theory was originally applied in somewhat different form by Condon, Altar and Eyring[22], in that the zero-order wave functions were taken as those for the three-dimensional harmonic oscillator, and the perturbing potential taken as that due to the field of the dipole moments assigned to the different bonds. Such calculations

were applied to methyl phenyl carbinol nitrite, the calculated rotatory contribution of the nitrite absorption band being used to assign the absolute configuration implied by the Fischer projection formula



to the levorotatory isomer. A magnitude of the same order as that deduced for this bond from rotatory dispersion measurements was obtained. However the same sort of calculation applied to sec-butyl alcohol gave a calculated rotation several hundred times too small. The Eyring school has since abandoned this procedure in favor of that previously described.

Part III Present status of the problem of absolute configuration

Waser[49] has given arguments leading to an absolute configuration of tartaric acid based on correlation of the crystal structure of tartaric acid as determined by Beevers and Stern[50] and the observed crystal habit, using qualitative arguments as to the expected rate of growth of crystal faces as affected by the number and ease of formation of intramolecular hydrogen bonds. Schomaker[51] however has pointed out that the crystal habit used by Waser in his deductions is that from the aqueous solution, where solvent

molecules may be expected to compete with tartaric acid molecules for the hydrogen bonding sites on the crystal faces. It is therefore not obvious from a discussion involving only tartaric acid molecules which faces will tend to grow more rapidly. The result obtained by Waser for the absolute configuration of dextrorotatory tartaric acid is shown in Figure 10, where the heavy lines

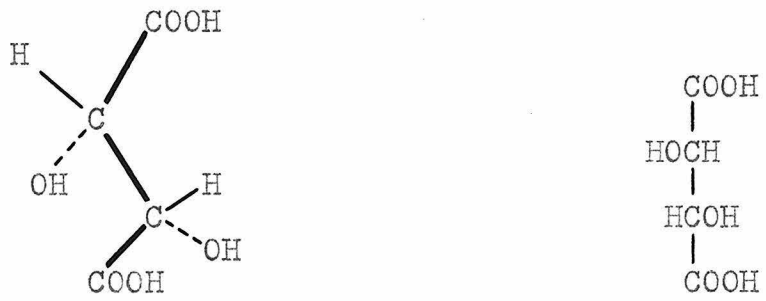


Figure 10. Left, absolute configuration of dextrorotatory tartatic acid according to Waser. Right, the projection formula of the isomer on the left according to the Fischer projection convention.

lie in the plane of the paper, the light solid lines point upwards, the dotted lines downwards. The planar <u>trans</u> conformation of the four carbon atoms is that found by Beevers and Stern; no attempt has been made to show in Figure 10 the orientations of the carboxyl groups with respect to their rotations around the bonds to the neighboring carbon atoms as found from the x-ray studies. Figure 10 also shows the projection formula of this isomer according to the Fischer

projection convention. The result is opposite to the absolute configuration obtained for tartaric acid on the basis of Fischer's assumption regarding the absolute configuration of glucose.

Summarizing the results obtained for the absolute configurations, the calculations of Kuhn, those of Eyring and his co-workers, and those of the present work on 2,3-epoxybutane all agree in finding the same absolute configurations as those currently in use by organic chemists, namely, those derived from Fischer's original assumption of an absolute configuration for dextrorotatory glucose and the relative configurational studies of organic chemistry. These results disagree with the deduction of Waser described above.

The result of Kuhn is open to objection as to the correctness of the molecular conformation assumed, as well as on other points as discussed above. The absolute configurations assigned by Eyring and his co-workers have the advantage of internal consistency with the relative configurational data of organic chemistry, but are nonetheless open to question as to the conformations assumed, certain details of the calculations, and the adequacy of the general approximations introduced. A check of the consistency of the g theory, or first-order polarizability theory, awaits completion of the experimental work described in the previous section.

It is interesting to point out <u>apropos</u> of the Eyring

one-electron theory that its application to the compounds trans-2,3-epoxybutane and propylene oxide with the same sort of approximations as introduced in the treatment of sec-butyl alcohol would lead to the calculated optical activity of the butylene oxide being only twice that of the propylene oxide. No term corresponding to the interaction of the two methyl groups appears. Inasmuch as the experimental rotation of the butylene oxide is far different from this predicted value it must be concluded that a calculation of this sort would be inadequate for a discussion of the rotatory power of trans- 2,3-epoxybutane. While this argument cannot be said to definitely prove the one-electron contributions to be unimportant, inasmuch as higher approximations can be introduced so as to bring in a methyl-methyl term, nevertheless it is necessary to observe that there is no apparent reason why the methyl-ethyl interaction in sec-butyl alcohol should be of a smaller order of magnitude (barring unfavorable orientations) than the methyl-methyl interaction in trans-2,3-epoxybutane. Thus it must be considered probable that in the calculation of Gorin, Walter and Eyring for sec-butyl alcohol important contributions have been omitted. Moreover it seems very likely that the omitted terms are of the $g^{(0)}$ type.

SECTION V

MOLECULAR STRUCTURE OF 1,2 DICHLOROPROPANE VAPOR AS DETERMINED FROM ELECTRON DIFFRACTION AND FROM ANALYSIS OF DIPOLE MOMENT DATA

Part I: Electron Diffraction Investigation

This investigation was undertaken in order to obtain structural information particularly with respect to the internal rotation around the 1,2 carbon-carbon bond, for the calculation of the optical activity according to the theory of Section III. Only one structure determination has been reported in the literature, that of Berger[52] using x-ray diffraction from the gaseous molecules. He assumed approximate values for the bond distances and tetrahedral bond angles, and reported satisfactory agreement between his intensity measurements extending to $q = 22$ (for definition of q, see below) and theoretical intensities calculated with the hindering potential $V(\varphi) = \frac{V_o}{2}(1-\cos\varphi)$, $V_o = 0.88$ kcal/mole, being the angular displacement between C-C-Cl bond planes, taken as zero at trans. Considering the low accuracy of the x-ray method applied to gases, it seems clear that these results should not be taken as conclusive. The structure of the related molecule 1,2-dibromopropane was determined by Schomaker and Stevenson[41] using electron diffraction methods. They reported the molecule to have normal values for the bond distances and bond angles, and to have a root mean square

torsional vibration of $\pm$ 20° around the trans position.

Two independent samples were used in the experiments. Sample I was the commercial Paragon product which had been redistilled through a short packed column. It had a boiling range 95.6 to 96.4° C, $n_D^{25°}$ 1.4367. Sample II was prepared from propylene glycol in this laboratory by Dr. H. K. Garner: b.p. 96.3 to 96.4° C, $n_D^{25°}$ 1.4368. These values, particularly those for Sample II compare favorably with those recently reported by Dreisbach and Martin(55), namely b.p. 96.2° C, $n_D^{25°}$ = 1.43638. The diffraction apparatus has been described by Brockway(54). The camera distance used in this investigation was about 11 cm. for Sample I, while with Sample II photographs were taken at both 11 cm. and 20 cm. The wavelength of the electrons was about 0.06 Å. The photographs which were utilized in the measurements and in the drawing of the visual curves were made with the gas near room temperature.

The two sets of photographs closely resembled each other for the most part, those of Sample II being in general clearer. Measurements of the diameters of the apparent maxima and minima were made on both sets, corrections being made for film expansion. Differences between the measurements on two sets appeared where the pictures of the first set were very diffuse and difficult to observe, and also on the outer rings, where those of the second set were much easier to observe. There were no systematic

differences between the two sets, or between the long and short camera sets with Sample II.

Figure 11 shows the visual curve V_1 as drawn from the photographs obtained from Sample I. In the course of our use of the correlation method certain difficulties experienced in fitting theoretical intensity curves with V_1 made it seem likely that several features had been erroneously interpreted. This was borne out by the independent observations of a third person, an experienced observer, Dr. Kenneth Hedberg of this laboratory. The changes arising from these considerations have been incorporated into visual curve V_2, as well as other changes resulting from observation of the more distinct photographs of Sample II. In V_2 the depth of minimum 2 compared to minimum 3, the height of maximum 2 compared to maximum 3, the position of shelf 4 on maximum 3, and the position of shelf 9 on maximum 10 represent reinterpretations in line with the views of the third observer. The relative depths of minima 6 and 8 represent a compromise between the opinions of different observers; the feature is difficult to observe as regards this point. The relative heights of the maxima 11, 12, and 13, and the shape and measurements of minima 19 and 20, and maximum 19, represent changes arising from observation of the second set of pictures. The last mentioned features were already difficult to observe; beyond them the appearance seemed to be that indicated, but

the exact appearance was very uncertain.

The radial distribution curves RDI_1 and RDI_2 shown in Figure 11 were calculated from V_1 and V_2, respectively, using the equation

$$r\,D'(r) = \sum_{q=1,2\cdots}^{q_{max}} I(q) e^{-aq^2} \sin \frac{\pi}{10} qr \qquad (138)$$

and the usual punched card methods[55,56,57]. The convergence factor a was so chosen that $\exp(-aq^2) = 0.10$ at $q = 100$. Well defined peaks are seen to occur at the distances expected for the C-C, C-Cl, C...Cl, and Cl...Cl bonds in the molecule*: in RDI_1 at 1.56, 1.82, 2.73 and 4.32 Å respectively; in RDI_2 at 1.53, 1.81, 2.72 and 4.30 Å, respectively. In both curves the C-H peak is distorted by low frequency errors. The small, rather undulatory peaks of about one-tenth the height of the major ones may in some cases correspond to minor distances in the molecule, but may also be caused by errors in drawing the visual curves. The peak at 2.72 Å is appreciably broadened, corresponding to a temperature factor $a_{C\ldots Cl}$ (defined below) somewhat less than 10^{-4}, or to a symmetrical splitting of the three distances with separations about 0.05 Å on either side of the central

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* A connecting dash indicates a bonded pair; dots, a non-bonded pair.

value. The peak at 4.30 Å is broadened also, indicating some motion of the chlorines. Perhaps the most striking feature of the radial distribution curves is the high value obtained for the C-Cl distance, some 0.04-0.06 Å larger than the usual value. The discrepancy is greater than is to be expected to arise through error, and there can be little doubt that the C-Cl bond is at least slightly longer than found in the chlorinated methanes. The C-C peak is not well resolved, and its position provides no certain indication of the distance in the molecule. Consequently the bond angles and, more interesting for the present study, the angle φ specifying the internal rotation are not accurately determined. The latter has been defined in Section III. The indeterminacy in φ resulting from the indeterminacy in C-C is illustrated in the following calculation: if we set C-Cl = 1.81, C···Cl = 2.72, Cl···Cl = 4.30, then C-C = 1.50 gives $\varphi = 27^{\circ}$, while C-C = 1.60 gives $\varphi = 18^{\circ}$.

It is perhaps not out of place to include a few remarks on the relationships to be expected between radial distribution curves obtained by use of equation (138) and the actual probability distribution of an internuclear distance depending on an internal rotation as typified by the present instance. For the sake of simplicity we will suppose that the contribution $I_{A-B}(q)$ of this distance to the total scattering I(q) has somehow been isolated from the latter,

and further that it has been determined exactly within a range of scattering angle $0 \leqslant q \leqslant q_{max}$. In our discussion we shall ignore the dependence of the x-ray form factors on q (see below). Under these conditions the actual probability distribution function $r^2D(r)$ and the scattered intensity are related by the equation

$$I_{AB}(s) \propto \int_0^\infty rD(r) \sin rs \, dr ,$$

$$s = \frac{\pi}{10} q , \tag{139}$$

which may be inverted to give

$$rD_{AB}(r) \propto \int_0^\infty I_{AB}(s) \sin rs \, ds . \tag{140}$$

Because the conditions of the experiment do not permit the observation of I(s) for s greater than a certain maximum, resort is had to the introduction of the convergence factor previously mentioned, a new function rD'(r) being defined as

$$rD'(r) \propto \int_0^\infty I_{AB}(s) \, e^{-a's^2} \sin rs \, ds ,$$

$$a' = \frac{100a}{\pi^2} . \tag{141}$$

The Fourier folding theorem then gives as the relationship between rD(r) and rD'(r)

$$rD'(r) \propto \int_{-\infty}^\infty r'D(r') \, e^{\frac{-(r-r')^2}{4a}} \, dr' . \tag{142}$$

Thus the effect of the introduction of the convergence factor for the case when the distance AB is completely rigid is to give rD'(r) the form of a gaussian peak instead of the ideal delta function corresponding to rD(r); the position of the peak of the former corresponds, however, to the position of the latter. If rD(r) is itself a gaussian due to thermal motion of the atoms A and B with a Hooke's law force, rD'(r) becomes a gaussian of somewhat greater width, the peaks of both being located at the same value of r. With more complicated forms of rD(r), especially with asymmetric rD(r), the relationship between it and rD'(r) becomes more complex; in particular, the positions of the modes of the two distributions will no longer coincide. As an example, in the case of a torsional oscillation in such a molecule as propylene chloride with the <u>trans</u> position as the mode, the peak of the radial distribution function obtained from equation (138) does not correspond to the <u>trans</u> value of the distance, even in such an ideal case as that just discussed. Sample calculations indicate that a difference of the two modes of as much as 0.05Å or more might result in a typical case. Values of the angle calculated from the Cl.....Cl peak in the RDI do not, therefore, have necessarily any direct significance in terms of the angular coordinate of the mode of the actual probability distribution of the distance.

Turning now to the minor distances in the molecule, moderately heavily temperature factored distances are expected near 2.16 Å and 2.45 Å corresponding to the non-bonded C···H and Cl···H pairs having a common ligand. The C···C term occurs near 2.52 Å with even smaller amplitude (about one-seventh of that of the C-Cl term). For $|\varphi| < 30^\circ$ a small and possibly very heavily temperature factored term due to the rotation dependent C···Cl occurs in the range 2.8-3.5 Å. If the internal rotation (torsion) is appreciable, the peak may well be missed entirely. A variety of other terms due to hydrogen interactions exist in the molecule but would not be expected to appear in the RDI.

The distortion of the C-H peak is not unusual in molecules as complicated as this. It was thought nevertheless desirable to investigate more closely these obvious errors, particularly when certain points in the correlation treatment required a comparison of nonadjacent features of the visual curve as to their relative heights and depths. To this end a peak corresponding to the position and shape expected for C-H was sketched in, as shown by the dotted curve in V_2 at this neighborhood. The difference between this and the RDI actually obtained was treated as a correction, Fourier-inverted, and the result (after modification to allow for the use of the convergence factor) considered as a correction V_2' to visual curve V_2. There are presumably other errors in the RDI, but because of its unique low frequency

character, we consider this to be of particular interest. The positive hump in V_2' at small q corresponds to a rather obvious but not too important mistake in drawing V_2. Other than this, and of great interest, there is the negative peak in the region of maxima 18 and 19. All observers were agreed that the relative intensities of the pair of maxima 14 and 15, maximum 17, and the pair 18 and 19 were as drawn in V_2. But great difficulty was found in fitting this with models acceptable otherwise. This, combined with the negative correction obtained in V_2', lead us to believe that an error in interpretation was made. This is not too surprising, since at such large scattering angles observation is difficult; also the disturbance of the edge of the film begins to be bothersome there.

In the course of our application of the correlation method it became desirable to consider the possibility of moderate temperature factors in the C···Cl and Cl···Cl distances due to vibrational modes (in addition to the torsional mode in the latter case). Thus we were led to look into the normal coordinate analysis of simpler related molecules. In past electron diffraction investigations it has been usual to assume a rigid heavy atom skeleton unless large amplitudes of vibration were obviously to be expected, or unless the assumption made it impossible to obtain a fit. The latter was the case with the C···Cl distance in the

present investigation. But it is possible for confusion to arise from the existence of a Cl···Cl temperature factor of this sort: the attenuation which it produces in the amplitude is comparable to that of a reasonably large rotational libration. Failure to differentiate between the two may result in erroneous values for the potential hindering internal rotation. The situation is perhaps not as bad as appears at first sight, since the difference in the intensity dependence is quite marked for librations about trans; consequently if the calculations are performed carefully the effect may in some cases be detected. In practice, however, this point seems not to have been noticed; the investigation of propylene bromide by Schomaker and Stevenson[41], of ethylene chloride by Beach and Palmer[58] and by Yamaguchi, Morino, Watanabe and Mizushima[59] are examples where the possibility of such an effect was not discussed.

Normal coordinate analyses of trans 1,2-dichloroethane have been published by Mizushima and Morino[60]. Because these authors did not require for their purposes the complete determination of the forms of vibration which is necessary for the calculation of the temperature factors, we have repeated their calculations (neglecting the motions of the hydrogens as in their first paper) using the same force constants and obtaining the same frequencies. For the averages of the squares of the displacements from the

equilibrium position we obtained $\overline{\Delta r^2_{C-Cl}} = 0.0030$, $\overline{\Delta r^2_{C-C}} = 0.0026$, $\overline{\Delta r^2_{C\ldots Cl}} = 0.0063$ and $\overline{\Delta r^2_{Cl\ldots Cl}} = 0.0070$. Calculation of the temperature factors defined in equation (143) below then gave after reduction by a constant amount such as to make $a_{C-C} = 0$: $a_{C-Cl} \approx 0$, $a_{C\ldots Cl} = 0.00018$, $a_{Cl\ldots Cl} = 0.00020$.

The skeletal motion in ethyl chloride was subjected to normal coordinate analysis by Cross and Van Vleck[61]. We have very crudely estimated the temperature factors from the frequencies and diagrams of the normal modes given by them with the result, again referred to $a_{C-C} = 0$: $a_{C-Cl} \approx 0$, $a_{C\ldots Cl} = 0.00027$. These calculations seem to indicate but of course do not prove (because of the question of the adequacy of the simple valence force potential assumed) that temperature factors of a moderate magnitude are possible for these molecules. For obvious reasons we have not attempted a normal coordinate analysis of 1,2-dichloropropane. However it seems reasonable that a similar order of magnitude might occur in corresponding distances.

Proceeding now to the discussion of our use of the correlation method we first list the various terms followed by a number indicating the approximate relative scattering weight. Of bonded pairs there are two C-C, 19; two C-Cl, 45; six C-H, 17. Of nonbonded pairs which are bonded to a

common atom there are one C...C, 6; three C...Cl, 45; seven C•••H, 10; three Cl•••H, 11. There are two important distances depending on the internal rotation: Cl•••Cl with weight 27 at <u>trans</u>, and the C•••Cl, weight 13 for the same configuration. The remaining interactions are hydrogen-hydrogen, or hydrogen with a carbon or chlorine not bonded to its ligand. These have a total weight of very roughly 45.

Theoretical intensity curves were calculated using punched card methods[56,57]. In all the calculations unless otherwise specified C-C was fixed at 1.54 Å. The selection of optimum values for the other parameters determines the shape of the molecule, the actual size being then calculated from the scale factor (average of q_{calc}/q_{obs}). Except where otherwise stated the following assumptions have been made: both C-C's equal, both C-Cl's equal, three C•••Cl's equal. In the case of the last, however, it should be mentioned that we found it necessary to apply a small temperature factor to the term, as is made plausible by the normal coordinate analysis mentioned; consequently, we could also explain our results with three rigid C•••Cl distances symmetrically distributed with separation of about 0.05 Å. We have assumed the C-C-C bond angle to be tetrahedral, and also all bond angles (insofar as we have considered the interactions concerned) involving hydrogen to be tetrahdral.

Furthermore we have neglected the contribution of the hydrogen-hydrogen terms to the scattering, as well as the terms involving hydrogen and carbon or chlorine when the latter are not attached to the carbon bonding the hydrogen concerned. The total weight of these neglected terms is perhaps impressive, but it must be remembered that they undoubtedly have severe temperature factors due to the bending and stretching motions of the hydrogens and, in the case of the second variety mentioned, depend also on one or both of the internal rotations. An approximate calculation, using reasonable values for the hydrogen force constants and frequencies, assuming no rotation around the 1,2 C-C bond but free rotation of the CH_3 group, gave a contribution for these terms which damped out very rapidly, decreasing to one-tenth at q = 35; the changes in the theoretical intensity curves even at smaller scattering angles were rather minor. In the calculation just mentioned, and all the following calculations of intensity curves, we have used $a_{C-H} = 0.00016$, $a_{C\cdots H}$ and $a_{Cl\cdots H} = 0.00030$.

With the above assumptions the remaining shape parameters may be taken as 1) C-H; 2) C-Cl; 3) C···Cl; 4) positions of the minima of the potential hindering internal rotation around the 1,2 C-C bond; 5) shape of the potential barriers, especially in the neighborhood of the minima; 6) skeletal vibrational temperature factors.

The appropriate equation for the intensity function is

$$I(q) = \frac{1}{\overline{(Z_i - f_i)(Z_j - f_j)}} \sum_{\substack{i,j \\ i \neq j}}{}' \frac{(Z_i - f_i)(Z_j - f_j)}{r_{ij}} e^{-a_{ij}q^2} \sin \frac{\pi}{10} r_{ij} q \ ,$$

$$a_{ij} = \frac{\pi^2}{200} \overline{\Delta r_{ij}^2} \ .$$

(143)

The sum is over all the pairs of nuclei in the molecule, r_{ij} being the distance separating nuclei i and j. Z_i is the atomic number, f_i the x-ray form factor for nucleus i. In the first equation the bar indicates an average over all pairs of nuclei. In the second equation the bar indicates the statistical average in the equilibrium ensemble. Use of the factor $\exp(-a_{ij}q^2)$ implies the assumption of simple harmonic motion. Where the latter assumption is not permissible, the factor $\frac{1}{r_{ij}} e^{-a_{ij}q^2} \sin \frac{\pi}{10} r_{ij} q$ must be replaced by $\int r_{ij} D(r_{ij}) \sin \frac{\pi}{10} r_{ij} q \, dr_{ij}$, $r_{ij}^2 D(r_{ij}) \, dr_{ij}$ being the probability that atoms i and j are to be found a distance apart between r_{ij} and $r_{ij} + dr_{ij}$, and the integral being over the range of variation of r_{ij}. In the calculations reported here the x-ray form factors have not been included, inasmuch as trial calculations showed the changes occurring on their inclusion to be rather minor.

The internal rotation was first treated on the assumption that but one significant potential minimum is present,

and that the form of the potential may be sufficiently well represented by $V(\varphi) = \frac{Vo}{2}\left[1-\cos(\varphi-\varphi_o)\right]$. The effect of the possible existence of other minima is described later.

The correlation of the theoretical curves is to be done with V_2; it is necessary to bear in mind, however, that there will in general be a range of acceptability for each feature. Examples of this will be mentioned in the course of the description below. The number of parameters involved, as well as the complicated nature of some of them, permit no more than give a rather brief summary of the work.

It was not found possible to find acceptable correlations with models having a single rigid C•••Cl distance. The features primarily requiring a temperature factor in this term were the tripled maxima 11, 12, 13 and the doubled maxima 18 and 19; however it is possible to fit both of these features with a rigid C•••Cl, the difficulty being that other features cannot be made acceptable.

Theoretical intensity curves are shown in Figures 11 and 12, the parameters being given in Table 3. Curves D1, D2 and D3 of Figure 11 illustrate the effect of varying the equilibrium angle φ_o while retaining the same "barrier height" Vo and other shape parameters. Of the features which vary considerably with this change we may discuss particularly the relative amplitudes of maxima 6 and 7, which are seen to be quite sensitive to this variation. A best

value of φ_o, subject to the arbitrary assumption of the other shape parameters is easily chosen. To illustrate our differentiation between acceptability and nonacceptability for this particular feature, we mention that in D1 and D3 we regard it as being unacceptable, while D2 is quite good. An important and interesting effect is evident in these three curves, namely, the amount of attenuation of the Cl···Cl term varies, although Vo is the same for all. This is due to the rather rapid increase of $\frac{dr}{d\varphi}$ as φ increases from zero. The maximum of $r_{Cl...Cl}$ as a function of φ at $\varphi = 0$ has a further result in that the probability distribution of distances is asymmetrical. The effect of this may be roughly described as follows: given an asymmetrical distribution of distances, in which there is a single mode which does not coincide with the average, the "effective value" of the distance for small scattering angles is the average; at large scattering angles it is approximately the mode, the transition taking place gradually. The attenuation of the amplitude increases as the range of distances included in the range of highly probable values of φ increases. Thus for a given value of Vo, with φ_o at trans the asymmetry is at a maximum, and the deviation of the effective value of $r_{Cl...Cl}$ in the first part of the scattering pattern from the mode (which is the trans value) is at a maximum. With φ_o away from trans the range of variation of the effective value of the distances decreases, while the

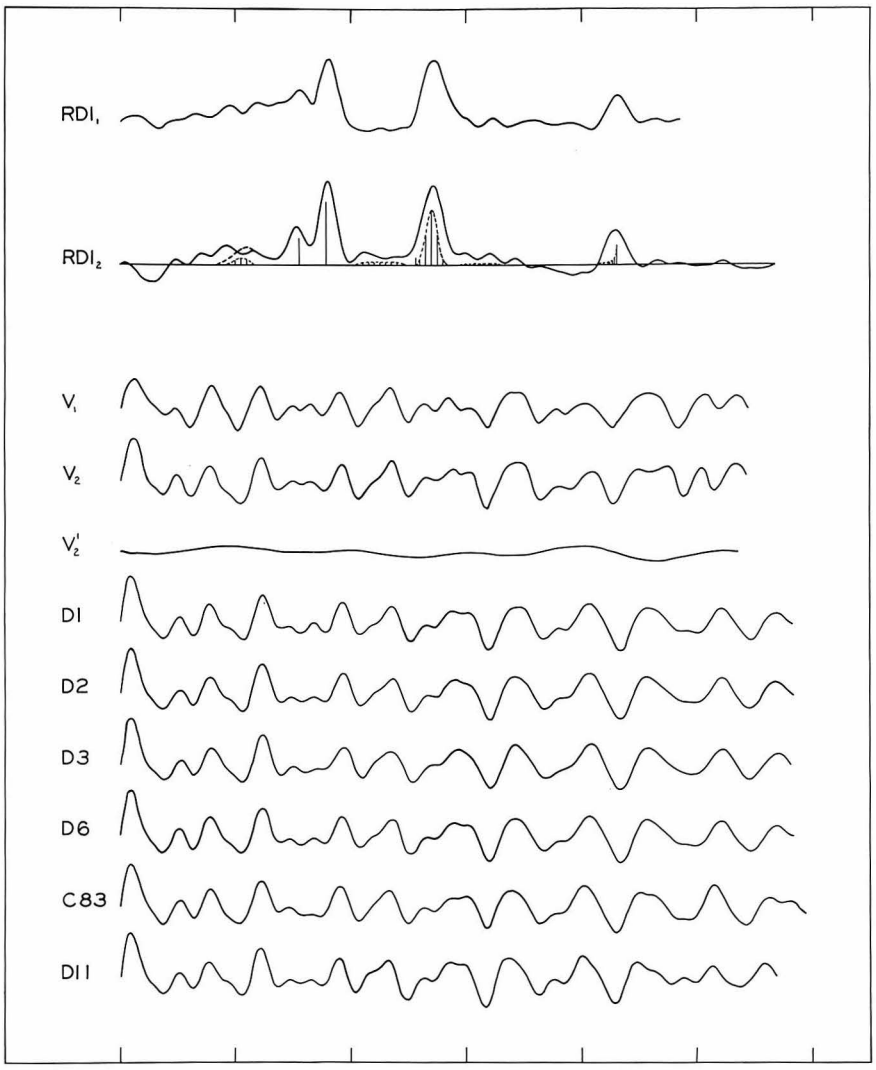

Figure 11 Radial distribution, visual and theoretical intensity curves.

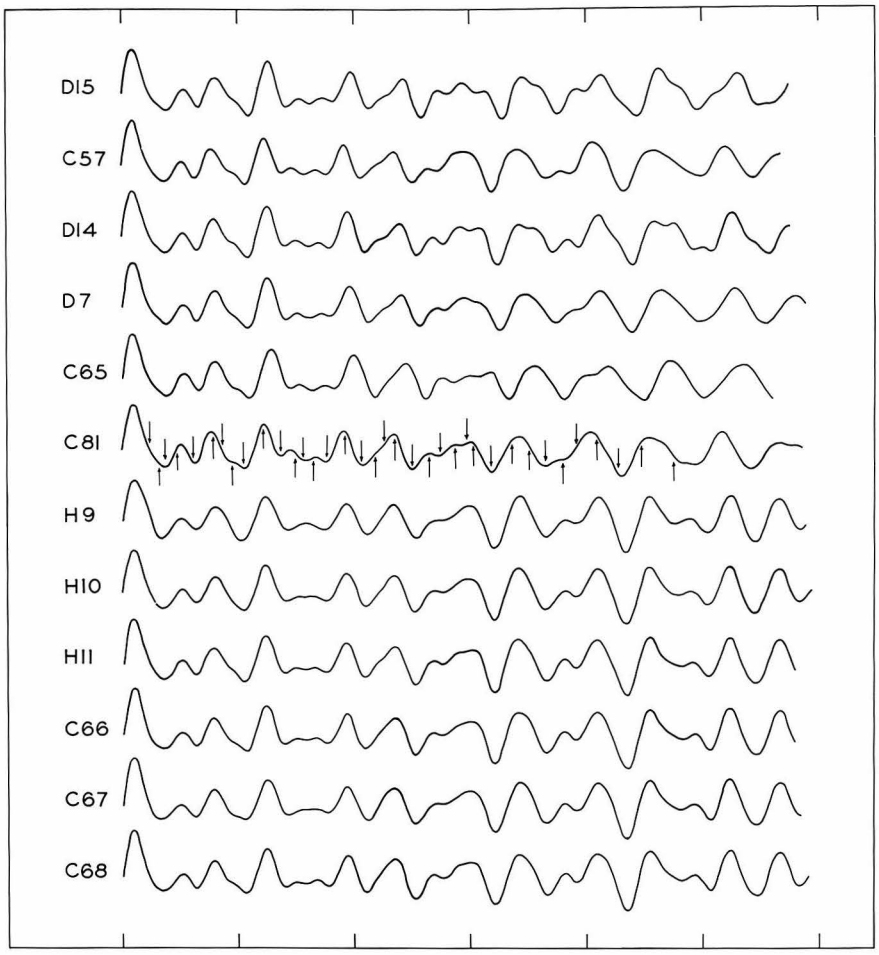

Figure 12 Theoretical Intensity Curves

TABLE 3

Distances* and angles in the models of Figures 11 and 12

Model	C-Cl	C...Cl	V_o, $\frac{kcal}{mole}$	φ_o degrees	$a_{C...Cl}$	$a_{Cl...Cl}$
D1	1.79	2.70	30	-10	0.00010	0.00010
D2	1.79	2.70	30	-20	0.00010	0.00010
D3	1.79	2.70	30	-30	0.00010	0.00010
D6	1.79	2.70	10	0	0.00010	0.00010
C83**	1.80	2.73	4	0	0.00010	0
D11	1.82	2.74	60	-25	0.00010	0
D15	1.76	2.64	60	-20	0.00010	0
C57	1.79	2.72	30	-20	0.00010	0.00010
D14	1.76	2.68	60	-15	0.00010	0
D7	1.76	2.66	30	-20	0.00010	0.00010
C65	1.73	2.60	30	-15	0.00010	0.00010
C81**	1.80	2.73	10	0	0.00010	0.00010
H9	1.79	2.70	30	-20	0	0
H10	1.79	2.70	30	-20	0	0
H11	1.79	2.70	30	-20	0	0
C66	1.79	2.70	--	---	0	0
C67	1.79	2.70	--	---	0	0
C68	1.79	2.70	--	---	0	0

* C-C and C-H 1.54 and 1.09, respectively, unless otherwise noted.

** C-C = 1.57; C-H = 1.06.

attenuation of the amplitude increases for the same Vo. Thus there is a rather subtle interaction of the parameters Vo and φ_o. An example of this can be seen in Figure 11: although curve D1 with Vo = 30 kcal/mole and $\varphi_o = -10^o$ is unsatisfactory because $|\varphi_o|$ is too small, curve D6 with $\varphi_o = 0^o$ and Vo = 10 kcal/mole is acceptable. Curve C83 with $\varphi_o = 0^o$ and Vo = 4 kcal/mole is unacceptable.

We have investigated a corresponding range of angles for a series of values of both C-Cl and C···Cl, using a simple device to investigate the effect of varying C-H where this appeared worth-while. As described above one soon obtains a qualitative understanding of the nature of the interdependence of Vo and φ_o, so that the order of magnitude of Vo may be anticipated. Thus for angles greater than about 30°, no satisfactory curves were found; for angles near 20°, Vo in the neighborhood of 30 kcal/mole is satisfactory; for the trans position, V_o in the neighborhood of 10 kcal/mole is required. Curves for different combinations of C-Cl and C···Cl are shown in the figures, the best value of φ_o having been already chosen for each combination.

It is convenient first to discuss the curves in regard to the shape and size of the doublet maxima 18 and 19. Thus in D2, D11, and D 15 the feature lacks the proper shape required by our interpretation, maximum 19 being not sufficiently pronounced relative to maximum 18. In C57 the shape is

satisfactory, but the overall height of the feature somewhat small. The shape is also satisfactory in D14, and the size somewhat improved. If C-Cl is chosen as low as 1.73 Å and C···Cl then selected so as to give a satisfactory shape to maxima 18 and 19, there is then no choice of φ_0 which makes the inner features, particularly maxima 6 and 7, satisfactory. If a somewhat larger C···Cl distance is chosen (same C-Cl) the situation is reversed; there seems to be no satisfactory choice with C-Cl this small. For C-Cl equal to 1.82 Å and greater the curves have satisfactory shapes at these two features, but the height of maxima 18 and 19 decreases. Other defects arise also: the tripled maxima begin to degenerate into a high doublet on the outside, and a small, separated inside member.

In all the curves which we have so far called acceptable, there are in one respect or another certain deficiencies associated with the height of maximum 10 relative to that of maximum 8 and the tripled maxima 11, 12 and 13, with the depth of minimum 9 relative to that of minima 8 and 11, and with the depth of minimum 11 relative to that of minima 9 and 14. Two experienced observers both gave as their opinion that maximum 10 should be higher than the line joining maximum 8 and the triplet, minimum 9 deeper than the line joining minima 8 and 11, and minimum 11 shallower than the line joining minima 11 and 14; in each case the limit of acceptability was thought to be the tangency of the feature

and the line. This requirement is already a revision of the original observation, which implied more stringent requirements. These were concerned with the relative amplitudes of pairs of adjacent features: thus, maximum 10 was interpreted as being higher than maximum 8. It is indeed difficult to avoid this interpretation of the photographs. However we regard an observation of this kind as being easily in error due to the difficulty of estimating sufficiently accurately the behaviour of the effective background. The comparison of three adjacent peaks (or minima) we regard as being more reliable. We were led to make this reinterpretation by difficulties in fitting the first type of observations.

Thus, as regards maximum 10, curves C83, D6, D11, D15 are barely acceptable, curves D2, D14, C57 unacceptable. Curves D2, D7, D11, C83, C57, D14, and C65 are barely acceptable or acceptable at minima 9 and 11. D15 is unacceptable at minimum 11, borderline with respect to minimum 9. No curve is everywhere satisfactory; D11, while satisfactory at the features just discussed, is not so at maxima 18 and 19. Models similar to D11, except in having a longer C•••Cl (equal to 2.76 Å, say) are even better as regards maximum 10, as well as minima 9 and 11, and have a symmetrical doubled maximum 18-19, but the latter is rather too small to agree with our interpretation (even considering the correction V_2'), while the triplet suffers the deterioration of its shape previously mentioned. Also, the

height of the outer two of its members becomes equal to that of the following doublet (15-16). The observations give distinctly the impression that the following doublet is the stronger; however our understanding of the visual process would suggest that this is a natural type of misinterpretation if the triplet feature may be considered as a general maximum of greater width than the doublet.

Curves with still larger values of C-Cl (1.85 Å) were calculated, but cannot be regarded as satisfactory because of an accentuation of the defects already commented upon for C-Cl = 1.82 Å, and other defects as well: maximum 9 occurs too far up on maximum 10, and maximum 13 tends to become higher than 12.

Finally, in the hope of relieving the difficulties which have just been described we have investigated briefly the effect of varying C-H. The difficulty at maximum 10 may be removed or reduced by shortening C-H to 1.04 Å or some intermediate value. Sometimes this will adversely affect the relations at minima 9 and 11, sometimes not. Such a change has appreciable effect only in the middle part of the scattering curve, becoming small at large scattering angles due to the temperature factor in the term.

As the best choice of shape parameters subject to the assumption of a cosine barrier with a single minimum we give C-H = 1.04, (C-C = 1.54), C-Cl = 1.76, C···Cl = 2.67, $0 \leq |\varphi_o| \leq 25^\circ$; $V_o \geq 4$ kcal/mole; $a_{C\ldots Cl} = 0.00010$. There is

not sufficient difference between the curves calculated for different values of φ_o provided an appropriate choice of V_o is made, to justify a choice among them. For $\varphi_o = 0$, V_o = 10 kcal/mole; for $\varphi_o = -25°$, V_o = 30-40 kcal/mole are optimum values. For the larger values of V_o (and $|\varphi_o|$) a temperature factor $a_{Cl\cdots Cl} = 0.00010$ is helpful, to remove a hump on the outside of maximum 17 which does not correspond to the observation. It also results in the coalescence of maxima 18 and 19 into a single broad maximum, but this we regard as entirely compatible with our observation. For lower values of Vo, for which φ_o must be at or near <u>trans</u>, inclusion of such a Cl···Cl temperature factor results in but little change in the optimum choices of the parameters. In many of our calculations we have not included this temperature factor because of the amount of labor involved.

The application of an interpolated scale factor to the values just chosen gave C-H = 1.06, C-C = 1.57, C-Cl = 1.80, C···Cl = 2.73; C81 is the curve for this model. Table 4 shows the comparison of the q values of the maxima and minima calculated from this model with the observed values. The average value of q_{calc}/q_{obs} deviates from unity due to uncertainty in the interpolation. The distances in this model after correction with the average of q_{calc}/q_{obs} are shown with their relative weights in RDI_2, where the dashed boundaries indicate temperature-factored distances. The distances thus calculated are not the optimum values due to the fact

TABLE 4

Observed and calculated positions of apparent maxima and minima

Max	Min	q_{obs}*	q_{calc}(C81)	q_{calc}/q_{obs}**
	1	4.6	4.2	(0.913)
1		6.2	5.8	(.935)
	2	7.4	7.4	(1.000)
2		9.5	10.1	(1.063)
	3	12.2	12.6	(1.033)
3		15.6	15.4	0.987
	4	17.2	18.2	(1.058)
4		19.0	19.8	(1.042)
	5	20.9	21.0	1.005
5		24.3	24.4	1.004
	6	27.3	27.4	1.004
6		29.9	29.0	0.970
	7	31.2	31.6	1.013
7		33.0	33.4	1.012
	8	35.3	35.0	0.992
8		38.4	37.3	0.971
	9	41.2	41.4	1.005
9		43.7	43.1	0.986
	10	45.1	44.6	.989
10		47.0	46.9	.998
	11	50.0	50.0	1.000
11		53.0	52.6	0.992
	12	54.8	54.5	.994
12		57.5	57.2	.995
	13	59.4	58.7	.988
13		60.6	60.5	.998
	14	63.6	63.8	1.003
14		67.3	66.8	0.992
	15	68.8	68.3	.993
15		70.2	69.8	.994
	16	73.0	73.0	1.000
16		76.0	75.5	0.993
	17	78.3	77.0	.983
17		81.8	80.2	.980
	18	85.6	86.3	1.008
18		89.6	89.9	(1.003)
	19	92.4	91.5	(0.990)
19		95.2	93.1	(.978)

ave: 0.995 ± 0.008
Scale factor* = 0.993

* The values of q_{obs} were calculated from the ring measurements using a tentative wave length of 0.0608 Å. The value of the wavelength interpolated from calibrations preceding and following the experiment is 0.06065. This decreases the scale factor to $0.995 \times \frac{0.06065}{.0608} = 0.993$.

** The parenthesized figures were omitted from the averaging.

that the wave length 0.0608 used in computing q_{obs} from the measured ring diameters is somewhat larger than the value 0.06065 indicated by calibrations. Use of the scale factor obtained in this way, and consideration of the expected limits of error in the size determination as well as of the range of acceptability of the shape parameters give as the optimum values C-C = 1.56 Å, with limits 1.49-1.60 Å; C-Cl = 1.79 ± 0.035 Å; C···Cl = 2.71 ± 0.025; $V_o \geq 4$ kcal/mole; $|\varphi_o| \leq 30^\circ$, with the previously discussed correlation in the optimum values of V_o and φ_o. It is difficult to choose best values of Vo and φ_o ; those of C81, viz. Vo = 10 kcal/mole, $\varphi_o = 0$ are as good as any. We refrain from reporting a determination of C-H, since except for the finer points of interpretation which have been mentioned, the scattering is not very sensitive to its variation. We have indication of errors in the visual curve corresponding to this distance in the distorted appearance of the C-H peak in the RDI. Its small weight, short distance, and temperature factor combine to make it rather inaccessible to the electron diffraction-visual method. The difficulty in obtaining a really good fit to our observations is also an indication of error in the estimation of the delicate intensity relations, and it does not seem likely that the rather close choice of the C-H value which is best really corresponds to an accurate determination. Indeed, it would seem unlikely that the C-H distance is much different from 1.09 Å.

The uncertainty in the sign of φ_o indicated by the absolute value signs arises because the only important term which depends on the sign is the odd C···Cl, with an amplitude for a rigid molecule of about half that of Cl···Cl. The values of Vo which have been seen to be necessary result in very heavy temperature factors for this term since it, unlike Cl···Cl, is well removed from its extremal values for the required values of φ_o. For Vo = 30 kcal/mole and φ_o near trans, the C···Cl term has decreased to one quarter of its initial value at q = 35. This initial value being itself small, the term has little effect. For smaller Vo, it is even less important. For larger Vo, tending toward rigid models, the term becomes more important, and indeed, for the larger values of the magnitude of φ_o the positive sign is unsatisfactory. We have not made a detailed investigation of the question of the upper limit of Vo, primarily because its exact value is not of particular importance in the computation of the optical activity. The longer persistence of the C···Cl term for very large Vo results in these values tending in general to be somewhat unsatisfactory. It seems a priori likely if the equilibrium position departs from trans, that it will be displaced towards negative φ_o, due to the repulsion between the CH_3 and Cl. The van der Waals' radii of methyl and chlorine are approximately equal; if the repulsions are sufficiently similar, the conformation would be expected to be like that of 1, 1, 2-trichloroethane, for

which Turkevich and Beach reported a displacement of about 10° in the corresponding direction[62].

The above limits on C-C are considerably larger than any likely variation of the distance from the covalent bond distance 1.54. Because of this uncertainty, the value of the C-C-Cl bond angle varies over a wide range also: taking the central values for C-Cl and C···Cl and the extremes for C-C, the corresponding range for this bond angle is 111.3°-106.2°; the quoted optimum C-C distance gives 108.0°.

Thus far the correlation method has been based on the assumption of but one significant minimum of the potential. We wish now to investigate the effect of the existence of other minima. That such exist would be predicted from the work of Gwinn and Pitzer[45] on ethylene chloride, and the configuration found for 1, 1, 2-trichloroethane by Turkevich and Beach[62]. We believe the importance of staggered configurations over eclipsed to have been sufficiently well established to rule out appreciable contributions of the latter compared to the former for temperatures of interest here. Considering the work just mentioned we regard the three most likely isomers to be: the <u>trans</u> or near-<u>trans</u> form, which has already been considered; the <u>gauche</u> or skew form in which the CH_3 is <u>trans</u> with respect to the Cl (equivalent to skew isomer of ethylene chloride if H replaces CH_3); the "staggered <u>cis</u>" in which the H of the $CH(CH_3)Cl$

group is trans with respect to the Cl of $-CH_2Cl$. We suppose that in the latter the steric repulsions are sufficiently large to render it unstable relative to the other two for temperatures of interest, as was found to be the case in the corresponding isomer of 1, 1, 2-trichloroethane (ΔE 2500 cal/mole) by Thomas and Gwinn[63]. If the net reactions concerned are repulsive, as seems likely, then we expect the weight of the skew isomer to be intermediate between half the value found for ethylene chloride (0.1) and that for trichloroethane (0.5). As is apparent from the discussion of Section III, in order to obtain an unambiguous sign for the calculated optical activity it is necessary to place an upper limit on the amount of the skew isomer present. Our treatment of the problem is directed toward this end.

The amount of labor involved and the result obtained with the approximate treatment to be described have led us not to make a detailed examination of this parameter along with the rest. Rather we have simply performed a few calculations for various relative amounts of the two isomers by adding the corresponding curves in the appropriate ratios. In the discussion to follow we will for brevity refer to the near-trans isomer as simply the trans isomer, for which we have used the parameters of model D2, except that we have not included the C···Cl temperature factor previously mentioned. While this model is not the best final choice, it is sufficiently close to make the results reliable. We

approximate the hindering potential in the neighborhoods of the trans and the gauche minima by separate one-fold cosine barriers. For the values of the parameters used in the calculations the intersections of the two barriers occur at energies high enough to make the exact manner of their joining inconsequential. The parameters of the one-fold cosine barrier in the neighborhood of the gauche minimum will be indicated by V_{og} and φ_{og}.

Curves H9, H10 and H11 represent just the basic trans model, but with the amplitudes of the rotation-dependent terms 25%, 50% and 75%, respectively, of their actual values. The utility of these curves lies in the fact that for reasonable values of Vo at the gauche minimum the Cl···Cl contribution decreases rapidly to a small value at quite small scattering angles. The rotation dependent C···Cl distance, it is true, is now at its maximum value, and so retains its initial amplitude for some time; however the latter is now even smaller than before, due to the longer distance, being less than one-third of the Cl···Cl amplitude. Its effect is not large. These three curves allow us to place a limit on the amount of gauche present. Thus H9 is so unsatisfactory as to rule out a 75% contribution of gauche. H10, 50% gauche, is questionable at many points and is probably rejectable. H11, with 25% gauche, is as satisfactory as the 100% trans curve.

Turning now to curves containing specific gauche terms C66 composed of 75% of the basic trans conformation and 25% of a gauche conformation with V_{0g} = 30 kcal/mole and φ_{0g} = -120°, is acceptable. Its similarity to H11 illustrates the rapid diminution of the C···Cl term already mentioned. C67, which is 50% gauche with V_{0g} = 30 kcal/mole and φ_{0g} = 120°, is at least as unsatisfactory as H10. C68, containing 25% gauche with V_{0g} = 80 kcal/mole and φ_{0g} = -120° has a difficulty in the relation between maxima 6 and 7; this however can be rectified by a slight change in φ_0 for the trans model and the curve is probably satisfactory. Smaller values of $|\varphi_0|$ for the gauche model also help. Other values of the parameters were also tried; in general no essential improvement results on including the gauche. Amounts between 0-25% seem equally acceptable for reasonable V_{0g}. Amounts of 50% or more are not compatible with the electron diffraction experiment. It does not seem possible to set the upper limit of the amount of gauche much lower than this on the basis of the electron diffraction experiment.

It should be mentioned that though we have quoted the barrier heights on the basis of cosinusoidal potentials, the actual calculations have been for the most part made with quadratic potentials having the same curvature at the minimum as the quoted sinusoidal value. The two potentials agree satisfactorily up to energies high enough to make the procedure essentially equivalent to use of the cosinusoidal barriers.

Part II Analysis of dipole moment data

It has been seen that the electron diffraction method is able to show clearly that at least half, and probably more, of the molecules may be assigned to the trans minimum. However, it is desirable to investigate more closely the magnitude of the gauche contribution. Possible sources of additional data are the dipole moment and its temperature dependence, as well as infra red and Raman spectra. The dipole moment of the vapor over the temperature range 340 -500° K has been determined by Oriani and Smyth[64]. We are grateful to these authors for making available to us their data before publication. Their dipole moment values are shown in Table 5, as well as values calculated from their polarization measurement using a different treatment of the atom polarization P_A. Their calculation was made setting $P_E + P_A = M_{R_D}$, P_E being the electronic polarization, M_{R_D} the molar refraction for the sodium D line. We have estimated P_E from M_{R_D} by utilizing the correction resulting upon extrapolation of M_R to infinite wavelength in the case of the related compound ethylene chloride, and estimating P_A as 10% of P_E. The difference between the two sets, while significant with respect to the value of the dipole moment at a given temperature, is nearly constant through the range of measurements, and affects only the value used for the bond moment in the calculations to follow. This latter value must

TABLE 5

Dipole moment of propylene chloride from the data of Oriani and Smyth[64]

Temp. ^{o}K	Dipole moment as calculated by Oriani and Smyth $u \times 10^{18}$	Dipole moment calculated using an alternative value of P_A $u \times 10^{18}$
344.7	1.46	1.40
381.7	1.50	1.44
393.8	1.53	1.47
432.2	1.59	1.52
465.6	1.63	1.56
505.7	1.68	1.61

be considered uncertain to an extent large compared to the differences here discussed, so that the choice of one or the other of the two sets of moment values makes little difference.

We shall first describe the assumptions we have made in discussing the relationship of the dipole moment and the internal configuration. These are: (1) that the group moments of the $-CH_2Cl$ and $-C(CH_3)HCl$ groups lie in their respective C-C-Cl bond planes, have the same magnitude, and make supplementary angles with the 1,2 carbon-carbon bond; (2) that these group moments move with the C-C-Cl bond planes as the molecule carries out its torsional motion around the 1,2 carbon-carbon bond, but remain constant as regards their magnitude and orientation within the bond planes. Under these assumptions the dipole moment of the molecule is given as a function of by the equation

$$\mu(\varphi) = 2\mu_{\perp} \sin \frac{\varphi}{2} \tag{144}$$

where $\mu_{\perp} = \mu_o \sin (\angle C\text{-}C\text{-}Cl)$, μ_o being the common magnitude of the moments of the groups.

Inasmuch as the bonds to the two chlorines are not equivalent, the first assumption is not necessarily valid. The effects of induction will in general render the second also incorrect. It turns out however that most of the dipole moment is contributed by the gauche conformation, so that

the variability of $\mu_\perp$ should not be very serious; the value of $\mu_\perp$ obtained by correlation with the observed dipole moments will approximate its value at the gauche position. The effect of failure of the first category of assumptions would be to change the dependence of the total moment to the form

$$\mu^2(\varphi) = \left(\mu_\perp^{(1)} - \mu_\perp^{(2)}\right)^2 + \left(\mu_\parallel^{(1)} - \mu_\parallel^{(2)}\right) + 4\,\mu_\perp^{(1)}\,\mu_\perp^{(2)} \sin\frac{\varphi+\theta}{2} \tag{145}$$

where $\mu_\perp^{(1)}$ and $\mu_\perp^{(2)}$ represent the projections of the two bond moments onto a plane perpendicular to the 1,2 C-C bond, and $\mu_\parallel^{(1)}$ and $\mu_\parallel^{(2)}$ represent the components parallel to the 1,2 C-C bond. The angle θ is a constant determining the departure of the orientation of zero dipole moment from the position $\varphi = 0$ (trans). Providing that the magnitudes of the bond moments differ by no more than 0.10 Debye units, the effect of the first two terms will not be large. The displacement of the zero dipole moment position, if it is small compared with the uncertainties in the positions of the potential minima, will lead to no essential change; the temperature dependence of μ calculated from equation (145) with a potential of given shape with minima at φ_{ot} and φ_{og} will be the same as that calculated from equation (144) with a potential of the same shape and minima displaced by the amount θ. Inasmuch as neither the electron diffraction nor the dipole moment data (even without consideration of equation (145)) permit a precise determination of the positions of the minima, a small displacement of this kind will result simply in a change of

the optimum values of the barrier heights and positions of the minima, the new values in general lying within the range of uncertainty in the parameters.

Pitzer[65] has shown that in calculating the classical partition function the effects of the dependence of the vibrational frequencies and the external moments of inertia on the internal angle cancel each other, if the potential energy is free of cross terms between the vibrational coordinates and the internal angle. As a result one may use the simple weighting factor $\exp(-V(\varphi)/kT)$ in calculating classical averages of functions of the internal angle. Further, Gwinn and Pitzer[45] showed for ethylene chloride, where a detailed assignment of the vibrational frequencies of the two isomers is available, that the cancellation holds approximately in the quantum mechanical case. We shall suppose this to be also the case for the closely related propylene chloride.

If the gauche and trans minima were very narrow, bounded by very steep potential hills, the equation

$$\mu^2(T) = \frac{m_t^2 + m_g^2 a e^{\frac{-\Delta E}{RT}}}{1 + a e^{\frac{-\Delta E}{RT}}} \qquad (146)$$

would be valid, m_t and m_g being the moments in the trans and gauche configurations; a is the ratio of the statistical weights, depending on the form of $V(\varphi)$, and being roughly

measured by the widths of the two potential minima or by the vibrational frequencies; ΔE is the energy separation of the two minima. The equation may be conveniently put in the form

$$\ln \frac{m_g^2 - \mu^2(T)}{\mu^2(T) - m_t^2} = -\ln a + \frac{\Delta E}{RT} \qquad (147)$$

a plot of the left-hand side against 1/T should be a straight line. To make such a plot one must know values of m_g and m_t which depend on the bond moment and equilibrium angles. If we put $m_t = 0$ and choose various values of m_g we obtain the results shown in Figure 13. It is seen that the choice of different values of m_g does not influence the linearity very much, although the dependence is perhaps more nearly linear for the higher values of m_g. The value of a, determined by the intercept, is very sensitive, however. There is a slow systematic variation of ΔE, as given by the slope. The linearity is seen to be satisfactory if the measurement at the lowest temperature is disregarded; this discrepancy may be due either to inadequacy of equation (146), or to an erroneously high experimental value perhaps due to absorption on the condenser plates.

In the calculation just described, of the variables a, φ_g, $\mu_\perp$, and ΔE, the last is determined within not too large a range. The other three may vary within rather wide limits,

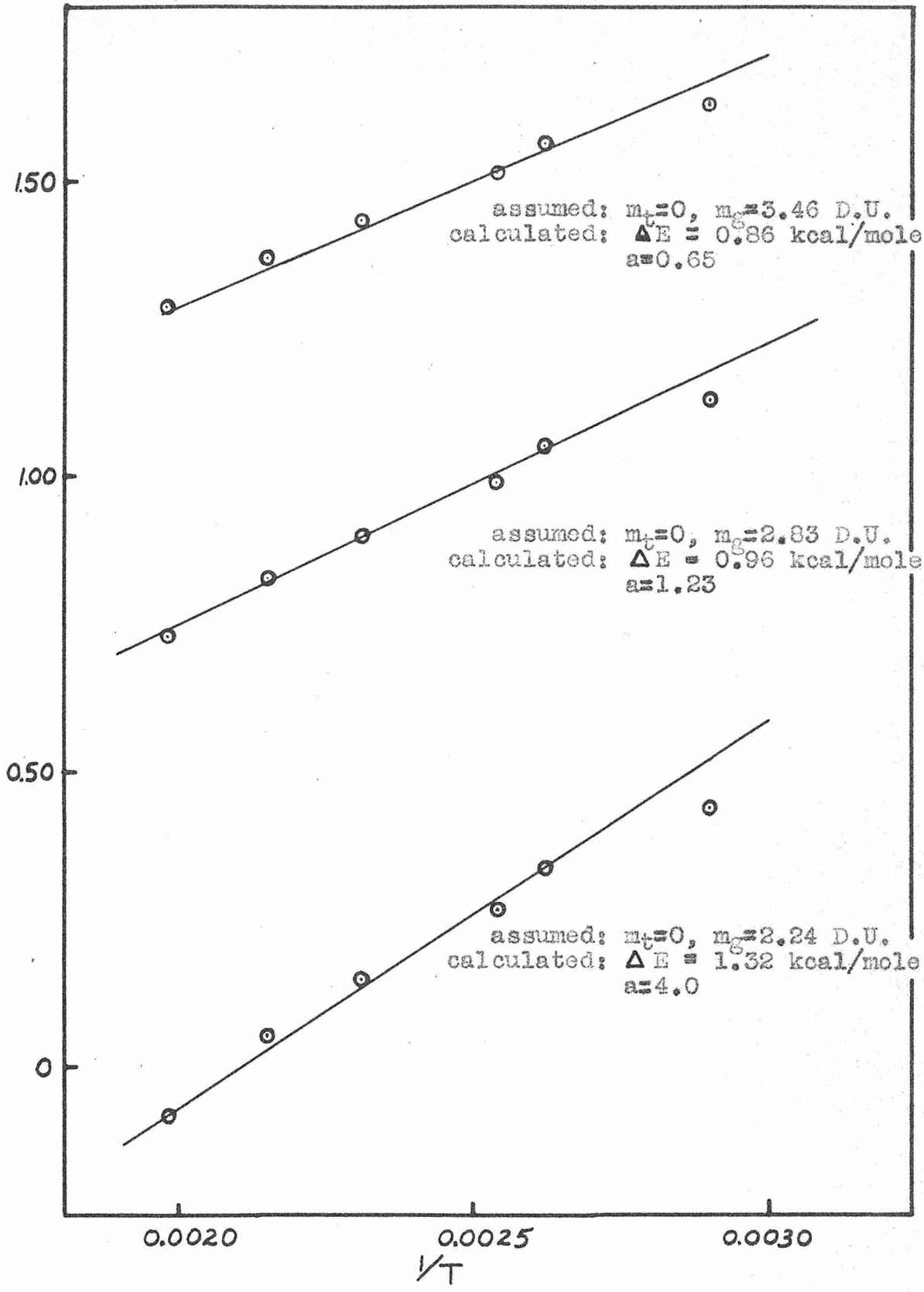

Figure 13. Plot of the left-hand side of equation (147) vs 1/T.

subject to the fact that if $\mu_\perp$ and φ_g are specified m_g is determined ($m_g = 2\mu_\perp \sin\varphi_g/2$), and a can then be determined from a graph as in Figure 13. To proceed further we need some further assumptions. The value of $\mu_\perp$ would be expected to be similar to that found by Gwinn and Pitzer[45] in ethylene chloride, namely, 1.59 D.U. It may however be larger due to induction in the CH_3 group, as is observed in ethyl chloride. It would hardly be expected to be this high, however, due to induction from the other C-Cl dipole. The ratio of statistical weights a would hardly be expected to differ much from unity - in ethylene chloride the corresponding ratio is approximately one, in 1,1,2-trichloroethane necessarily one. Steric repulsions may be expected to force φ_g slightly towards the <u>trans</u> position, away from its ideal value of -120°. The latter effect would probably not be any greater in propylene chloride than ethylene chloride, where a value very close to -120° was found to be satisfactory[45]. We have made some calculations for as large a displacement as $\varphi_g = -90^\circ$, which seems larger than would be expected. Table 6 shows the results of giving $\mu_\perp$ and φ_g values of the sort just discussed; the values of $\mu(T)$ used are those obtained by our treatment of P_A. Also shown are the specific rotations calculated using these statistical probabilities for the two conformations and curve C of Figure 4 and curve K of Figure 5 (Section III). If we consider $\varphi_t \neq 0$, so that $m_t \neq 0$, the chief effect is to lower the

TABLE 6

Average specific rotations and statistical probability of the gauche conformation according to equation (146)

Assumed			Calculated				
$\mu_\perp$	φ_t°	φ_g°	a	ΔE kcal/mole	Fraction of gauche at 300° K	$[\alpha]_D^{300°K}$ propylene chloride deg./dm.	$[\alpha]_D^{300°K}$ propylene bromide deg./dm.
1.59	0	-120	1.36	0.98	0.21	-39	-17
1.59	0	-90	3.60	1.36	.31	-34	-13
1.80	0	-120	0.86	0.88	.17	-44	-22
1.80	0	-90	1.86	1.04	.25	-40	-18
2.00	0	-120	0.64	0.84	.14	-47	-25
2.00	0	-90	1.18	0.92	.20	-45	-23
1.59	-25	-120	1.41	1.20	.16	-26	-4
1.59	-25	-90	3.53	1.44	.24	-24	-2

TABLE 7

Various potential barriers hindering internal rotation and the calculated average specific rotations

1. $V(\varphi)$ cal/mole $= \infty$	$40^\circ < \varphi \leq 180^\circ$
$= 5000/2\ (1-\cos\varphi)$	$-40^\circ \leq \varphi \leq 40^\circ$
$= 2100$	$-70^\circ < \varphi < -40^\circ$
$= \Delta E + 5000/2\ \ 1-\cos(\varphi+120^\circ)$	$-160^\circ \leq \varphi \leq -70^\circ$
$= \infty$	$-180^\circ \leq \varphi < -160^\circ$
E = 1.1 kcal/mole, $\mu_\perp$ = 1.76 D.U., $[\alpha]_D^{300^\circ K}$ = -35 deg/dm	
2. $V(\varphi)$ cal/mole $= \infty$	$40^\circ < \varphi \leq 180^\circ$
$= 30000/2\ \ 1-\cos(\varphi+20^\circ)$	$-50^\circ \leq \varphi \leq 40^\circ$
$= 2090$	$-80^\circ < \varphi < -50^\circ$
$= \Delta E + 5000/2\ \ 1-\cos(\varphi+120^\circ)$	$-160^\circ \leq \varphi \leq -80^\circ$
$= \infty$	$-180^\circ \leq \varphi < -160^\circ$
E = 1.3 kcal/mole, $\mu_\perp$ = 1.52 D.U., $[\alpha]_D^{300^\circ K}$ = -22 deg/dm	
3. $V(\varphi)$ cal/mole $= \infty$	$40^\circ \leq \varphi \leq 180^\circ$
$= 30000/2\ \ 1-\cos(\varphi+20^\circ)$	$-50^\circ \leq \varphi \leq 40^\circ$
$= 1640$	$-60^\circ \leq \varphi < -50^\circ$
$= \Delta E + 5000/2\ \ 1-\cos(\varphi+90^\circ)$	$-140^\circ \leq \varphi \leq -60^\circ$
$= \infty$	$-180^\circ \leq \varphi < -140^\circ$
E = 1.3 kcal/mole, $\mu_\perp$ = 1.74 D.U., $[\alpha]_D^{300^\circ K}$ = -27 deg/dm	
4. $V(\varphi)$ cal/mole $= V_1/2\ (1-\cos\varphi) + 440/2\ (1-\cos 3\varphi)$	$-150^\circ \leq \varphi \leq 30^\circ$
$= \infty$	otherwise
V_1 = 1.5 kcal/mole, $\mu_\perp$ = 1.83 D.U. (ΔE = 0.96), $[\alpha]_D^{300^\circ K}$ = -30 deg/dm	
5. $V(\varphi)$ cal/mole $= V_1/2\ (1-\cos\varphi) + 2200/2\ (1-\cos 3\varphi)$	$-180^\circ \leq \varphi \leq 60^\circ$
$= \infty$	otherwise
V_1 = 2.0 kcal/mole, $\mu_\perp$ = 1.62 D.U. (ΔE = 0.85), $[\alpha]_D^{300^\circ K}$ = -30 deg/dm	
6. $V(\varphi)$ cal/mole $= \infty$	$-10^\circ \leq \varphi \leq 180^\circ$
$= 0$	$-30^\circ \leq \varphi \leq -10^\circ$
$= 2100$	$-80^\circ < \varphi < -30^\circ$
$= \Delta E$	$-160^\circ \leq \varphi \leq -80^\circ$
$= \infty$	$-180^\circ \leq \varphi < -160^\circ$
E = 1.3 kcal/mole, $\mu_\perp$ = 1.29 D.U., $[\alpha]_D^{300^\circ K}$ = -12 deg/dm	
7. $V(\varphi)$ cal/mole $= \infty$	$0 < \varphi \leq 180^\circ$
$= 0$	$-40^\circ \leq \varphi \leq 0$
$= 2100$	$-80^\circ < \varphi < -40^\circ$
$= \Delta E$	$-160^\circ \leq \varphi \leq -80^\circ$
$= \infty$	$-180^\circ \leq \varphi < -160^\circ$
E = 1.1 kcal/mole, $\mu_\perp$ = 1.42 D.U., $[\alpha]_D^{300^\circ K}$ = -19 deg/dm	

value of a, for a given value of m_s, with little change in E.

The results obtained from the approximate formula are probably reasonably correct, the agreement with more refined calculations in the case of ethylene chloride being fair. However, it was thought worthwhile to perform a few calculations for more realistic barriers. We have assumed several different sets of values for the curvature and position of the two minima, leaving ΔE and $\mu_\perp$ as parameters to be fitted to the data. We have followed the procedure of choosing $\mu_\perp$ so that the calculated and experimental moments agree at 432° K, ΔE being adjusted so as to give the best correlation with the other temperatures. There seems to be no difficulty in obtaining acceptable fits over the rather small temperature range of the experiments, except for the behavior of the low temperature point previously mentioned. The results are given in Table 7, including the specific rotations calculated with these potentials and curve C' of Figure 4 (Section III).

The general behaviour may be summarized roughly as follows. To reasonably reproduce the observed temperature dependence of the dipole moment allowing for a possibly high experimental result at the lowest temperature, ΔE must be chosen in the neighborhood of $1000 \pm$ 200-300 cal/mole for values of the curvatures and positions of the minima within reasonable limits. The value of $\mu_\perp$ then depends on the positions and relative widths of the minima.

We have considered rather large widths of the gauche minimum relative to those of the trans minimum, although it seems unlikely that there would be much difference, as mentioned before. It is also to be noted that potentials 6 and 7 of Table 7, in which the gauche is respectively four times and twice as wide as the trans, result in too low values for $\mu_\perp$, and may for this reason be considered unlikely representations of the actual potential. The other potentials of Table 7 must be regarded as satisfactory representations of the electron diffraction (except potential 5, which has too narrow a minimum at the trans position) and of the dipole moment dependence, although potential 2 gives a value of $\mu_\perp$ which is approaching rejectable smallness. We believe that the range of potentials investigated suffices to give estimates of average values of quantities depending on the internal parameter which will be reasonable, but conservative in favor of avoiding an underestimation of the contribution of gauche.

In their paper Oriani and Smyth[64] have fitted potentials of the form $V(\varphi) = \frac{Vo}{2}(1-\cos\varphi), -\pi \leq \varphi \leq \pi$, to their dipole moment data, finding Vo = 2.5 kcal/mole. This value for a one-fold barrier is incompatible with the electron diffraction results. This contradiction is evidence favoring the existence of auxiliary potential minima, direct in the sense that no appeal to analogies with related compounds

are required, but indirect in the sense that it is not obvious that the existence of other minima is the unique resolution of the difficulty. It seems easy to understand why a potential of the form mentioned is a satisfactory form for the discussion of the electron diffraction, even when other significant minima are present, and at the same time leads to an erroneous answer when applied to dipole moment data. The dipole moment receives its important contributions from positions well removed from trans, even if their energy is quite high, due to the behavior of the function $\sin^2\varphi$. The electron diffraction pattern on the other hand, receives its predominant contributions from the positions close to trans.

The Raman and infra red spectra of the vapor have apparently not been investigated. It would be of great interest to study them, particularly their temperature dependence. The spectra of the liquid have been examined[67, 68,69] though not their temperature dependence, apparently. The liquid spectra show clearly the existence of at least two isomers in the same way as was noted in the case of ethylene chloride: see, for instance, the work of Mizushima[71] and his co-workers, which is summarized in the reference quoted.

Summarizing the results described in this section, the electron diffraction investigation of the structure of 1,2-dichloropropane has yielded the following structure parameters under the assumption of $V(\varphi) = \frac{V_o}{2} \quad [1-\cos(\varphi-\varphi_o)]$

for the potential hindering rotation; C-Cl = 1.79 ± 0.035; C...Cl = 2.71 ± 0.025; C-C = 1.56, limits 1.49-1.60; $V_o \geq$ 4 kcal/mole; $|\varphi_o| \leq 30°$, a small negative value being perhaps most probable, and where there is the previously discussed correlation between satisfactory values of φ_o and V_o. The effect of contributions of the gauche conformation was examined; the statistical probability of the latter is permitted by our interpretation of the data to have a maximum value of perhaps one-half. The diffraction pattern may be interpreted satisfactorily, with neglect of gauche contributions, however. Examination of published dipole moment data, subject to reasonable assumptions concerning the parameters involved, leads to a somewhat lower upper limit on the amount of gauche, of the order of one-fourth to one-third.

PROPOSITIONS

1. In the analysis of the temperature dependence of the dipole moment of a molecule such as ethylene chloride under the assumptions leading to equation (144) of this thesis, the further assumption of a one-fold sinusoidal hindering potential with minimum at the position of zero dipole moment (trans in the case of ethylene chloride) has been shown[70,71] to lead to the equations

$$\mu^2(T) = 2\mu_\perp^2(1-x) ,$$
$$x = -iJ_1(iV_0/2kT)/J_0(iV_0/2kT)$$

Here $\mu(T)$ is the observed moment, $\mu_\perp$ is defined as in this thesis following equation (144). V_0 is the barrier height. The functions appearing in the second equation are the ordinary Bessel functions of the first kind with imaginary argument, and are tabulated[72].

It may be noted that a very similar formula can be obtained when the potential minimum does not coincide with the position of zero dipole moment. If α is the angle between these two configurations, the first formula holds with the new definition

$$x = \frac{-iJ_1(iV_0/2kT)}{J_0(iV_0/2kT)} \cos\alpha .$$

2. It is proposed that the molecular structure of methyl-isopropyl ether be investigated by electron diffraction with particular attention to the internal rotation around the bond between oxygen and the secondary carbon of the isopropyl group. Designating the two equivalent staggered positions as the trans isomers, the third staggered configuration as

cis, there should be a good possibility of putting an upper limit on the relative amount of the latter present. It would be expected to be somewhat less than one-third. If this prediction is verified it will render doubtful the assumption of Rometsch and Kuhn[73] that in methyl-sec-butyl ether the conformation in which the methoxy group is trans with respect to the hydrogen bonded to C* is the most stable.

(3) The analysis of the temperature dependence of the rotativity (defined as $[\alpha]/n^2 + 2$) of sec-butyl alcohol recently published by Bernstein and Pedersen[74] is probably inadequate, in that only the internal rotation of the ethyl group around the 2,3 carbon-carbon bond has been considered. The rotation of the hydroxyl group may also be expected to influence the temperature dependence of the rotativity. The superposition rule used by these authors assumes the equilibrium positions to be in exactly the ideal staggered configurations, which is not required by symmetry.

(4) It is proposed that a possible one of the causes of a variation of the rotativity between liquid and vapor states is the occurrence of asymmetric molecular aggregates in the liquid state. The $g^{(0)}$ theory in principle would be suitable for calculation of such contributions, but the averaging process required is not practicable at present. Among other causes of such variations will be differences in internal conformation of the molecules in the two states, especially

in compounds having internal rotations.

(5) The resolution of 2,3-epoxy-2'-methylbutane and the determination of its configuration relative to trans-2,3-epoxybutane would afford an interesting test of predictions of the $g^{(o)}$ theory. The rotativity would be expected to be intermediate between those of the epoxybutane and propylene oxide, and isomers of the same sign of rotation should be configurationally related.

Also interesting in the same way but probably more difficult to carry out would be the resolution and determination of the relative configurations of trans-1,2-dichlorocyclopropane, 1,2,2'-trichlorocyclopropane and 1,1'-trans-2,3-tetrachlorocyclopropane. All should have the same rotativity values, and isomers having the same sign of rotation should be configurationally related.

(6) The parameter β of equation (43) of this thesis vanishes, inasmuch as the wave functions for the molecule in the absence of external magnetic fields may be taken as real. The second-order contribution of this term to the refractive index predicted by Condon[9] accordingly does not exist.

(7) It is proposed that an attempt be made to estimate the translational fluctuation correction to the Lorentz-Lorenz law, using methods analagous to those used by Kirkwood[26] in the case of the Clausius-Mosotti law. Experimental data[75] for argon at room temperature are available for comparison with theory. The term calculated in equation (83) of this thesis is a part of such a theory, but appears to

be too small to account for the observed effect.

(8) A phase diagram study of the arsenic-sulfur system is suggested. While it is not likely that stable compounds of lower sulfur content than As_4S_3 exist, this possibility would be worth investigation, as well as the general question of the nature of the changes accompanying the transformation of As_4S_4 to As_4S_6, and the latter to As_4S_{10}.

(9) A relation similar to the Silberstein[33] formula may be deduced from a set of zero-order wave functions similar to those introduced by Kirkwood[18]. Further terms are obtained, however which vanish only if special assumptions are made concerning the interacting groups. As would be expected, the classical and quantum mechanical expressions agree in the case of harmonic oscillators.

(10) If it be assumed that the molecular wave functions can be expressed as products of atomic wave functions, that portion* of the molecular magnetic susceptibility not due to spin and orbital angular momentum may be approximately expressed in terms of a sum of terms of the same form, one for each atom of the molecule. This may be taken as the theoretical explanation of the empirically observed rule of additivity of diamagnetic susceptibilities.

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* The quantity in question is that given by equation (11), p. 275 of J. H. Van Vleck, "Electric and Magnetic Susceptibilities", Oxford University Press, 1932.

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